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The Differential Diffusion Constants of Hydrochloric and Sulphuric Acids

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The differential diffusion constants of hydrochloric and sulphuric acids in aqueous solution at 25°C have been determined with Northrop-McBain diffusion cells. The range of concentration studied was 0.01–1.6 moles/liter for hydrochloric and 0.01–1.0 moles/liter for sulphuric. The relation previously proposed $k=k_0(1+c\partial \ln f/\partial c)\cdot(\eta_0/\eta)$ represents the variation of the diffusion constant with concentration reasonably closely, but the values of k_0 required to fit the experimental results are not those predicted by the Nernst relation.

IN 1937 it was suggested by one of us[1] that the variation in the differential diffusion constant k of a 1−1 electrolyte with concentration could be represented by the relation[2]

$$k=(k_0/2RT)\cdot(cd\mu_2/dc)\cdot(\eta_0/\eta), \qquad (1)$$

where k_0 is the value of k for infinite dilution, μ_2 is the thermodynamic potential of the solute at concentration c moles/cc, and η_0 and η are the viscosities of water and of the solution. The experimental data then existing (those of Clack[3] for KCl, NaCl and KNO_3, and of McBain and Dawson[4] for KCl) seemed on the whole to be consistent with Eq. (1), at any rate for moderate concentrations. (See reference 1 for a detailed discussion.) As a further test of the equation, we have measured the differential diffusion constants of hydrochloric and sulphuric acids at 25°C in aqueous solution; our reason for selecting these two electrolytes was that for both the mobilities of anion and cation are very different, and that in the case of sulphuric acid, the "thermodynamic factor," $(1/3RT)\cdot(cd\mu_2/dc)$ in this case, is in general far from unity.

The measurements were carried out using Northrop-McBain diffusion cells, and since the method has already been adequately discussed in the literature, no lengthy description is needed here. The cells were of about 100 cc capacity, and were of pore size G4; the general technique of the measurements was essentially that of Cole and Gordon,[5] except that the water bath containing the glass air baths was regulated to better than 0.01°, and that the preliminary diffusion required to set up a steady state in the diaphragm was only four hours. The final diffusion was allowed to proceed for from 45 to 70 hours depending on the magnitude of the diffusion constant. The cells were calibrated by allowing 0.1N KCl at 25° to diffuse into water; the value used for $\bar{k}$ for potassium chloride was 1.842×10^{-5} instead of 1.836×10^{-5} previously

[1] A. R. Gordon, J. Chem. Phys. **5**, 522 (1937).
[2] Very recently, P. Van Rysselberghe (J. Am. Chem. Soc. **60**, 2326 (1938)) has proposed independently a relation identical with our Eq. (1); we disagree with his discussion, however, in a few details, *vide infra*.
[3] B. W. Clack, Proc. Phys. Soc. **36**, 313 (1924).
[4] J. W. McBain and J. W. Dawson, Proc. Roy. Soc. **A148**, 32 (1935).
[5] A. F. Cole and A. R. Gordon, J. Phys. Chem. **40**, 733 (1936).

TABLE I. *Diffusion of* HCl *at* 25°C.

c_0'	c_0''	$((c_0'+c_0'')/2)^{\frac{1}{2}}$	$10^5 \cdot k_{obs}$	$F(f,\eta)$	$10^5 \cdot k_{calc}$
0.0218	0	0.104	3.00	0.957	3.00
.0312	0	.125	3.00	.951	2.98
.0542	0	.165	2.97	.943	2.96
.0573	0	.169	2.93	.943	2.96
.1143	0	.239	2.92	.935	2.93
.210	0.104	.396	2.95	.940	2.95
.273	.169	.470	2.97	0.951	2.98
.539	.416	.691	3.14	1.007	3.16
0.845	.727	0.887	3.46	1.086	3.40
1.090	0.935	1.006	3.61	1.144	3.59
1.299	1.208	1.120	3.76	1.209	3.79
1.353	1.246	1.140	3.87	1.219	3.82
1.713	1.539	1.275	3.95	1.301	4.08

proposed.[6] In general, the cells were recalibrated after every three or four runs with acid. As a rule no significant trend in the cell factor was observed, and consequently a simple average from all the calibrations was used in the final calculations. With two of the cells, however, there was evidence of a slight but definite increase in cell factor over a period of two years, and for these cells, the cell factors used were the average from calibration runs taken before and after the acid runs in question.

All analyses were carried out by means of a Rayleigh type interferometer, the comparison solutions having been made by gravimetric dilution from accurately analyzed stock solutions. The two-compartment interferometer cell was of brass, coated with Bakelite varnish, with optically flat glass windows, and was mounted inside the interferometer case in a heavy copper block, which served as a thermal shield. It has sometimes been reported that an interferometer will not yield reproducible results with relatively concentrated solutions. It has been our experience, however, at any rate for the concentration range in which we were interested, that if great care is taken to avoid any evaporation, either during the filling of the interferometer cell or during the actual measurement, it is possible to obtain results reproducible to better than 2×10^{-7} mole/cc; this was sufficient accuracy for our purpose.

Tables I and II summarize the results. Since the preliminary diffusion required to set up a steady state in the diaphragm results in values of the initial concentration inside the cell differing slightly from cell to cell, the first column of the tables gives the average value of c_0' (the initial concentration of the stronger solution) expressed in moles per liter; the second column gives c_0'', the initial concentration of the weaker solution in the outer compartment. The integral diffusion constant $\bar{k}$ for the concentration range in question is given by the McBain relation

$$\bar{k}=\{\log(c'+c''-2c_0'')-\log(c'-c'')\}/\beta\vartheta, \quad (2)$$

where c' and c'' are the inside and outside concentrations after the diffusion has been proceeding ϑ seconds, and β is the cell factor determined by calibration. The integral diffusion constant, computed by Eq. (2) from observed values of c', c'', c_0'' and ϑ, has been shown[1] to be (to a good approximation) the true differential constant k for the mean concentration $(c'+c'')/2=(c_0'+c_0'')/2$, provided $c_0'-c_0''$ is not too large. The third column of the tables gives the square root of the mean concentration, expressed in moles per liter.

Since there has apparently been some uncertainty[7] as to the concentration to which $\bar{k}$ refers, it is important to emphasize that the relation between k, $\bar{k}$ and the effective diffusion constant at any instant k', embodied in Eqs. (6) and (7) of reference 1, *viz.*

$$k'(c'-c'')=\int_{c''}^{c'} k\cdot dc \quad \text{(Eq. (6), reference 1)}$$

$$\bar{k}\vartheta=\int_0^{\vartheta} k'\cdot dt \quad \text{(Eq. (7), reference 1)}$$

TABLE II. *Diffusion of* H_2SO_4 *at* 25°C.

c_0'	c_0''	$((c_0'+c_0'')/2)^{\frac{1}{2}}$	$10^5 \cdot k_{obs}$	$F(f,\eta)$	$10^5 \cdot k_{calc}$
0.0211	0	0.102	2.10	0.751	2.16
.0483	0	.156	1.88	.699	2.01
.0513	0	.160	1.89	.696	2.00
.1051	0	.229	1.90	.656	1.89
.196	0.099	.384	1.80	.630	1.81
.358	.251	.552	1.85	.640	1.84
.508	.403	.675	1.88	.655	1.89
0.802	0.702	0.867	1.99	.683	1.97
1.102	1.006	1.027	2.22	.715	2.06
1.122	1.006	1.031	2.10	.716	2.06

[6] This value was obtained as described in reference 1, but is based on the recent thermodynamic data of T. Shedlovsky and D. A. MacInnes (J. Am. Chem. Soc. **59**, 503 (1937)).

[7] P. Van Rysselberghe (reference 2) assumes in effect (his Table II) that $\bar{k}$ is equal to k for a concentration c_0'; e.g. for 0.1*N* solution diffusing into water, he assumes that the measured integral constant is the true differential constant for 0.1*N*.

is valid regardless of the concentration range involved and of the exact functional dependence of k on c, provided one necessary and sufficient condition is fulfilled. This condition is that the concentration gradient in the diaphragm is at all times that for a steady state. Barnes,[8] in his rigorous solution of the problem, has shown that this is (to a good approximation) the case. Eq. (6) above, which is (strictly speaking) valid only for fixed c' and c'', is thus applicable to the diaphragm at every instant of the diffusion. Eq. (7) follows immediately from Eq. (6), where in (7), k' depends on t through its dependence on concentration; in Table III of reference 1, this dependence was evaluated roughly but closely enough. The rule that $\bar{k}=k$ for the mean concentration, on the other hand, is a cruder approximation, justified by numerical calculation in several rather unfavorable cases, and applicable only to narrow concentration ranges.

The fourth column of the tables gives the average value of k obtained from three or in most cases four independent measurements, each with a different cell. As a rule, the individual results showed a mean deviation from the average of one percent or less, although with the most dilute solutions the deviations were slightly greater. In a few runs, not recorded here, extremely erratic results were obtained, possibly caused by fluctuating temperature during some part of the experiment.

The thermodynamic factor can be expressed in several ways:

$$(1/\nu RT)\cdot(c\partial\mu_2/\partial c)=1+c\partial \ln f/\partial c, \quad (3a)$$

$$=(c/m)\cdot(1+m\partial \ln \gamma/\partial m)\cdot(dm/dc), \quad (3b)$$

$$=(V/n_1\bar{V}_1)\cdot(1+m\partial \ln \gamma/\partial m), \quad (3c)$$

$$=(V/n_1\bar{V}_1)/(1+0.018\nu m)+c\partial \ln f_r/\partial c, \quad (3d)$$

where ν is two or three for HCl and H_2SO_4, respectively, f, γ and f_r are the activity coefficients[9] on volume, molal and mole-fraction concentration scales, m is the molality, $\bar{V}_1$ is the partial molal volume of the solvent in the solution containing in V cc n_1 moles solvent and n_2 moles solute, and $c=n_2/V$. Eq. (3d) is suitable for hydrochloric acid, since the extended Debye-Hückel equation gives a convenient analytic representation for f_r, while Eq. (3c) is appropriate for sulphuric. For hydrochloric, the data of Shedlovsky and MacInnes[10] up to $0.1N$ and those of Harned and Ehlers[11] for higher concentrations were used; at $0.1N$, the two sets of measurements yield the same value of the thermodynamic factor within 0.1 percent. For sulphuric acid, the results of Harned and Hamer[12] were employed; these are intrinsically less accurate than are those for hydrochloric; moreover there is no convenient analytic representation for $\log \gamma$, and consequently the differentiation may of itself introduce errors. To effect the differentiation, a variety of methods, analytic, graphical and tabular, were employed, and from a comparison of the results, averaged values of the thermodynamic factor were prepared, which are probably not in error by more than 0.5 percent, at any rate for solutions stronger than tenth molal. The fifth column of the tables gives the values of the thermodynamic viscosity factor $F(f,\eta)=(1+c\partial \ln f/\partial c)\cdot(\eta_0/\eta)$ for the mean concentrations[13] of the experiments. All density and viscosity data required in the calculations are from *International Critical Tables*.

If Eq. (1) is valid, the ratio $k_{obs}/F(f,\eta)$ should be a constant equal to k_0; the average values of k_0 thus found are 3.135×10^{-5} for hydrochloric acid, and 2.88×10^{-5} for sulphuric. The last column of the tables gives the values of k obtained from these values of k_0 by the relation $k_{calc}=k_0\cdot F(f,\eta)$. With a few exceptions, the observed values agree with those calculated within the limits of error of the experiments.

[8] C. Barnes, Physics **5**, 4 (1934).

[9] In his discussion of the thermodynamic factor, P. Van Rysselberghe (reference 2) replaces f of Eq. (3a) by f_r; this is equivalent to replacing the first term on the right of Eq. (3d) by unity. This causes a negligible error in dilute solution, but is not always justifiable for higher concentrations; for example, for 25°, it will introduce an error in the thermodynamic factor of 1 percent for $2N$ KCl, of nearly 3 percent for $2N$ NaCl, and of 2 percent for $1.5N$ HCl.

[10] T. Shedlovsky and D. A. MacInnes, J. Am. Chem. Soc. **58**, 1970 (1936).

[11] H. S. Harned and R. W. Ehlers, J. Am. Chem. Soc. **55**, 2179 (1933).

[12] H. S. Harned and W. J. Hamer, J. Am. Chem. Soc. **57**, 27 (1935).

[13] The rule that $\bar{k}=k$ for the mean concentration is, in the case of sulphuric acid solutions less than tenth molal, a poor approximation, owing to the very rapid change of k with concentration for this electrolyte at high dilutions; a more refined calculation seems hardly justified, however, owing to the uncertainties in the thermodynamic data for sulphuric acid at low concentrations.

The interesting point is, however, that in neither case is k_0 identical with the limiting Nernst value. From MacInnes' data[14] for the limiting ionic mobilities, k_0 should be 3.335×10^{-5} for hydrochloric acid, nearly six percent greater than the result obtained here, while for sulphuric acid, if complete dissociation into hydrogen and sulphate ions be assumed, k_0 should be 2.55×10^{-5}, some 12 percent less than that found. It should be noted that Oholm[15] in his study of diffusion constants for electrolytes at high dilutions, found that the measured diffusion constant for HCl was noticeably less than the limiting Nernst value, while for the alkaline chlorides it was in reasonable agreement. Although the relation between Oholm's integral diffusion constants and the true differential constants is uncertain (because of the type of apparatus he used) it is significant that the deviation[16] he found is of the same sign and of the same order of magnitude as the one obtained here. In the case of sulphuric acid, which is a combination of a strong and a weak electrolyte, it might be expected that k_0, obtained as described above, should be different from that computed by the Nernst relation, although the sign of the deviation is surprising.

It must be admitted that all the values of k obtained in this research might be in error by the same constant factor if an erroneous value of $\bar{k}$ were used for the calibration. Thus the hydrochloric acid data would have been quite consistent with the Nernst limiting value if the diffusion constant chosen for the diffusion of $0.1N$ KCl into water had been 6 percent greater than the one actually used; this would imply, however, that McBain and Dawson's integral diffusion constants for the diffusion of $0.02N$ and $0.01N$ KCl into water (the differential constants for $0.01N$ and $0.005N$) were actually greater than the Nernst value for KCl, and that Clack's data (usually assumed to be reliable) were seriously in error.

If the Nernst relation is true for all electrolytes at infinite dilution, the only possible conclusion seems to be that at concentrations much lower than those studied here, there must be a dependence of k on c for these two electrolytes different from that predicted by Eq. (1). This much can be said, however: both hydrochloric and sulphuric acids differ from those previously discussed in that the difference in mobility of anion and cation is for them much greater than for KCl, NaCl and KNO_3; Eq. (1), considered as a purely empirical relation connecting the diffusion constant for one finite concentration with that for another finite concentration, seems to represent the data within the rather large limits of error inherent in such experiments.*

In conclusion, we would like to express our thanks to Mr. A. A. Janis of this department, who originally constructed the interferometer.

[14] D. A. MacInnes, J. Frank. Inst. **225**, 661 (1938).

[15] See Table 5 of J. W. Williams and L. C. Cady, Chem. Rev. **14**, 171 (1934).

[16] L. W. Oholm (reference 15) found for the ratio of the diffusion constants of $0.01N$ HCl and $0.01N$ KCl at 18°, 1.59. The ratio at 25° of k_0 for HCl to k_0 for KCl found here is $3.135/1.993=1.57$. If McBain and Dawson's data for KCl at 25° be recalculated on the assumption $\bar{k}$ for $0.1N$ KCl diffusing into water at 25° is 1.842×10^{-5} (the value used as our calibration), their integral diffusion constant for the diffusion of $0.02N$ KCl into water at 25° (the differential constant for $0.01N$) becomes 1.905×10^{-5}; this gives a ratio for the differential constants for $0.01N$ at this temperature also of 1.57. In view of the difference in apparatus and in temperature, this ratio agrees with Oholm's as closely as can be expected.

* *Note added in proof:* Since this article was submitted to the journal, a very important paper by Hartley and Runnicles has appeared dealing with the question of cell factor in the Northrop-McBain cell (G. S. Hartley and D. F. Runnicles, Proc. Roy. Soc. **A168**, 401 (1938)). By an entirely different method, they arrive at the conclusion that the "best" value of the ratio $\bar{k}/k_0$ for the diffusion of $0.1N$ KCl into water at 18° is 0.922. The value of $\bar{k}$ chosen here for the calibration gives for this ratio 0.924 at 25°; this corresponds to 0.925 at 18°, a result differing only by one third of one percent from their value. We wish to thank Professor Van Rysselberghe for calling this paper to our attention.

Spectroscopic Comparison of the Proton-Attracting Properties of Liquids

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The use of isotopic hydrogen has made possible an extension of the study of hydrogen bonds between unlike molecules to include many new types of donor solvents. From the magnitude of the shifts which the different solvents produce in the OD fundamental band of CH_3OD, a comparison of the proton-attracting properties of the different solvents can be made. It is suggested that this method may be used as a practical means of comparing the intrinsic strength of organic bases. Solvents representative of the classes—nitro-compounds, esters, aldehydes, ketones, ethers, nitriles and amines—were employed, and the results give proof of the wide occurrence of hydrogen bonding between unlike molecules.

IN previous communications[1] the author has submitted spectroscopic evidence for the association through hydrogen bonds of water, alcohol and certain other solutes, with many different electron donor solvents. In view of the remarkable success with which the hydrogen bond has met in the explanation of abnormal physical properties of numerous solutions,[2] an extension of these researches seems amply justified. The most pronounced effect of hydrogen bonding is that on the group which carries the hydrogen. Many donor solvents which may be expected to form hydrogen bonds with an OH group have bands in the region of 3μ. These make it impossible to ascertain the effects of the solvent on the absorption of this group. Fortunately, in the region of 4μ, where the OD fundamental of heavy water and heavy alcohol occurs, few solvents absorb appreciably. Hence the use of CH_3OD and D_2O in the present work has made it possible to study the proton-attracting power of a wider variety of solvents.

In general, the effects of hydrogen bonding on the OH or OD band are a shift to lower frequencies, a broadening and an increase in intensity. As has been previously pointed out by Fox and Martin,[3] from theoretical considerations, and by Badger and Bauer,[4] from a comparison of the frequency shifts of a few substances with bond energies obtained from a consideration of heats of vaporization, etc., there seems to be at least an approximate proportionality between the shift in frequency and the strength of the hydrogen bond.

INSTRUMENT

The instrument used was of the Wadsworth-Littrow type described by Strong.[5] With this instrument it was possible to resolve well the sharp monomolecular OD vibrational band of CH_3OD in inert solvents like benzene. One would not expect to observe fine structure in the spectrum of liquids, and, since one effect of hydrogen bonding is to broaden the OD band, little if any advantage would be gained by the use of a grating instrument of the type commonly used to study gases. Accurate calibration of the instrument is, of course, highly important. The CO_2 band occurring in the region studied was used to check the calibration each time a curve was run. The effective slit width in the region of 4μ was 0.025μ.

RESULTS

Inert solvents

The OD vibrational band which occurs in the liquid CH_3OD spectrum at 4.01μ, and which is very broad, occurs as a sharp band at 3.73μ for a sufficiently dilute solution of CH_3OD in

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[1] W. Gordy, Phys. Rev. **50**, 1151 (1936); **51**, 564 (1937); J. Chem. Phys. **4**, 769 (1936); J. Am. Chem. Soc. **60**, 605 (1938); W. Gordy and A. H. Nielsen, J. Chem. Phys. **6**, 12 (1938).

[2] E. N. Lassettre, Chem. Rev. **20**, 279 (1937); R. H. Ewell, J. Chem. Phys. **5**, 967 (1937); G. F. Zellhoeffer, M. J. Copley and C. S. Marvel, J. Am. Chem. Soc. **60**, 1337 (1938).

[3] J. J. Fox and A. E. Martin, Proc. Roy. Soc. **A162**, 419 (1937).

[4] R. M. Badger and S. H. Bauer, J. Chem. Phys. **5**, 839 (1937).

[5] J. Strong, Rev. Sci. Inst. **2**, 585 (1931).

benzene, Fig. 1. The band of the solution occurs very near that of the corresponding band of heavy alcohol vapor,[6] and is no doubt caused by CH_3OD in the monomolecular form. The differences of the liquid band from that of the solution is thought to be a result of association of the liquid through hydrogen bonds. Several experimenters have observed a similar effect for ordinary alcohol.[7] The curve for CH_3OD in bromobenzene is similar to that for the solution in benzene and indicates that there is no hydrogen bonding between the bromine of the solvent and the OD group. The solution curves given here are for $0.1M$, and the fact that no absorption occurs in the region of the associational band suggests that the CH_3OD exists almost if not completely in the monomeric form. A curve obtained for $0.2M$ CH_3OD in bromobenzene, which is not given, shows that the association is not completely broken down at this concentration.

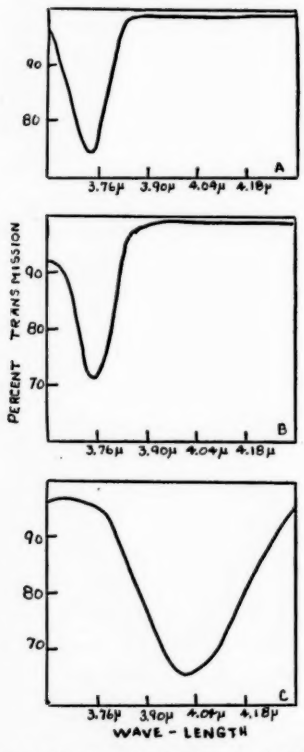


FIG. 1. The OD vibrational band of CH_3OD in: A. Benzene solution ($0.1M$, $t=0.32$ cm); B. Bromobenzene solution ($0.1M$, $t=0.32$ cm); C. Pure liquid.

[6] G. Bosschieter, J. Chem. Phys. **5**, 992 (1937).

[7] J. Errera and P. Mollet, Comptes rendus **204**, 259 (1937); J. J. Fox and A. E. Martin, Proc. Roy. Soc. **A162**, 419 (1937); E. L. Kinsey and J. W. Ellis, J. Chem. Phys. **5**, 399 (1937); A. M. Buswell, V. Dietz and W. H. Rodebush, *ibid.* **5**, 501 (1937).

Nitro compounds

For solutions of CH_3OD in nitrobenzene and in *o*-nitrotoluene the OD band appears at wavelengths only slightly longer than does the monomolecular band of the benzene solution. See Fig. 2, A and B. The curves shown are for concentrations of $1M$. A curve obtained for a $0.5M$ solution in nitrobenzene indicates that the position of the band remains constant for lower concentrations. The smallness of the shifts suggests that the hydrogen bonds between the CH_3OD and nitrobenzene and *o*-nitrotoluene, if indeed they may be classified as hydrogen bonds, are very weak. This is in accordance with the previous spectroscopic measurements[1] and with solubility measurements.[8] The shift produced by *o*-nitrotoluene is slightly greater than that for nitrobenzene.

Esters

The esters studied were ethyl acetate and amyl acetate, Fig. 2, C and D. The curves definitely indicate hydrogen bond formation in both cases, as was found true for CH_3OH in ethyl acetate and in ethyl formate.[9] The bonds formed with ethyl acetate seem to be slightly weaker than those with amyl acetate. From their data Zellhoeffer, Copley and Marvel[8] conclude that an ester group is approximately as effective as an ether group in increasing solubility. A comparison of the curve for CH_3OD in ethyl acetate with that for CH_3OD in di-ethyl ether shows that the ether produces a greater shift in the OD band. The shifts produced by the esters, however, are in the approximate order of those produced by the ethers.

Aldehydes

The previous spectroscopic studies of hydrogen bonds between dissimilar molecules[1] did not include aldehydes. There is evidence for chelation in *o*-hydroxy-benzaldehyde,[10] presumably due to

[8] K. von Auwers, Zeits. f. physik. Chemie **42**, 512 (1903); G. F. Zellhoeffer, M. J. Copley and C. S. Marvel, J. Am. Chem. Soc. **60**, 1337 (1938).

[9] D. Williams and W. Gordy, J. Am. Chem. Soc. **59**, 817 (1937).

[10] G. E. Hilbert, O. R. Wulf, S. R. Hendricks and U. Liddel, Nature **135**, 147 (1935).

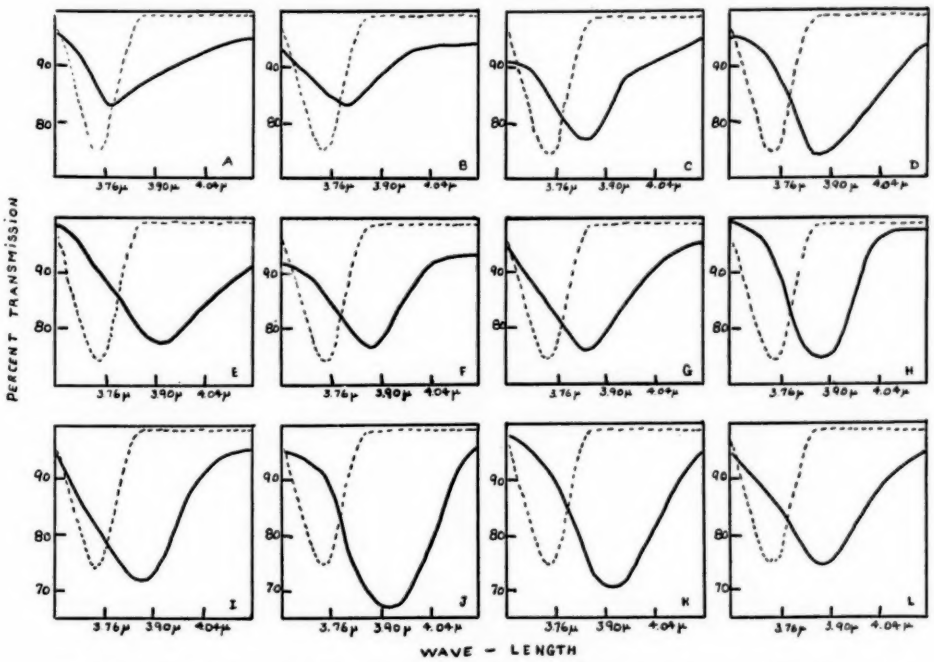


FIG. 2. Effects of association on the hydroxyl band. Broken line, 0.1M (t=0.32 cm) CH_3OD in benzene. Solid line, 1M (t=0.006 cm) CH_3OD in: A. Nitrobenzene; B. o-Nitrotoluene; C. Ethyl acetate; D. Amyl acetate; E. n-Butyraldehyde, F. Benzaldehyde, G. Methyl ethyl ketone; H. Acetone; I. Dioxan; J. Di-ethyl ether; K. iso-Propyl ether; L. n-Butyl ether.

hydrogen bonds between the OH and the aldehyde oxygen. The measurements here, which include one aliphatic and one aromatic aldehyde, suggest that an aldehyde oxygen is rather effective in forming hydrogen bonds, Fig. 2, E and F.

Ketones

Binary mixtures of acetone with alcohol, phenol, and other substances containing acceptor atoms have been widely studied by different physical methods, all of which point to marked complex formation.[1, 2] The results given here for CH_3OD-acetone mixtures are in complete agreement with the previous studies and show definitely that the complex formation is caused by hydrogen bonding. The behavior of methyl ethyl ketone is similar to that of acetone.

Ethers

Di-ethyl and iso-propyl ether produce the greatest shift in the OD band of any of the oxygenated solvents studied. The shifts produced by dioxan and n-butyl ether are only slightly less. It should be emphasized that the effects of the esters, aldehydes, ketones and ethers are all very similar.

Nitriles

Although the nitriles as solvents seem not to have been studied as widely as have certain oxygenated solvents, the previous infra-red studies[1] and the data reported here, Fig. 3, A and B, and Fig. 4, D, indicate that the nitriles are effective electron donor solvents. From the cases studied, using the shift produced in the hydroxyl band as a measure of the strength of the bonds, one would predict that the N of the nitrile group is almost as effective in bridging to a hydroxyl group as is the O of an ester group. Due to steric hindrance the iso-cyanides probably have much weaker donor properties. This is no doubt the reason CH_3CN is infinitely soluble in water while CH_3NC is only moderately soluble.

Amines

The amines are especially interesting in this study in view of the apparently conflicting data regarding complex formation involving some of

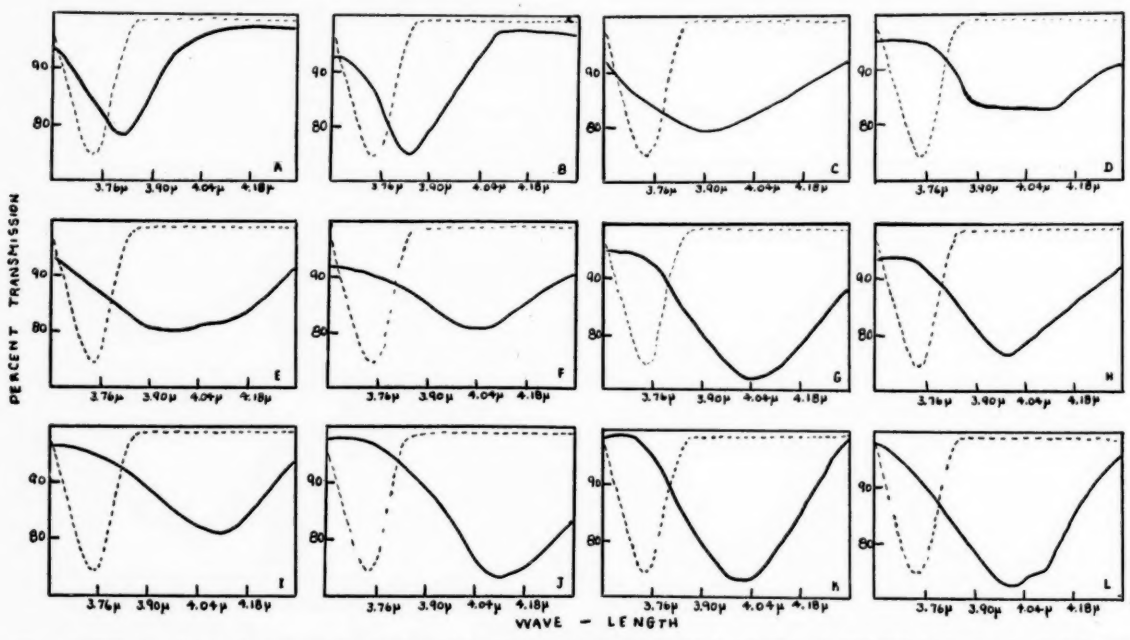


FIG. 3. Effects of association on the hydroxyl band. Broken line, 0.1M (t=0.32 cm) CH_3OD in benzene. Solid line, 1M (t=0.006 cm) CH_3OD in: A. Methyl cyanide; B. Benzyl cyanide; C. Monoamylamine; D. Di-*n*-propylamine; E. Monobutylamine; F. Di-*n*-butylamine; G. Tributylamine; H. Pyridine; I. Piperidine; J. Quinoline; K. *a*-Picoline; L. Nicotine.

the amines. Moore and Winmill,[11] as early as 1907, predicted from conductivity measurements that methyl amine in water solution exists largely in the hydrated form, while recently Edsall[12] has shown that the Raman spectra gives little evidence of such hydration. The NH absorption in the primary and secondary amines overlays the OH band, making it imperative that one component of the mixture be a deuterium compound. There is evidence[13] that the acceptor properties of the amine hydrogen is much weaker than those of the hydroxyl hydrogen. For this reason one would expect the hydrogen bonds between water or alcohol and an amine to be formed largely through the hydroxyl hydrogen. Of course, with the tertiary amines this would be the only possibility. Therefore, if hydrogen bonding occurs between the alcohols and amines, it should be evidenced through the effects on the hydroxyl band.

The most pronounced effects of any of the solvents on the OD band were found to be produced by the amines. Compare Figs. 2 and 3. For some of these the associational band appears at longer wave-lengths than the associational band in the pure liquid CH_3OD. The primary and secondary amines make the OD band exceptionally broad, and for some of these it appears double. This suggests a more complex association than the simple head-on type in which a single molecule, RNH_2, is linked through the hydroxyl group to a single alcohol molecule, XOH, as

$$\begin{matrix} & & H & & \\ & & | & & \\ R- & N & \cdots\cdots & H-O-X. \\ & & | & & \\ & & H & & \end{matrix} \qquad (1)$$

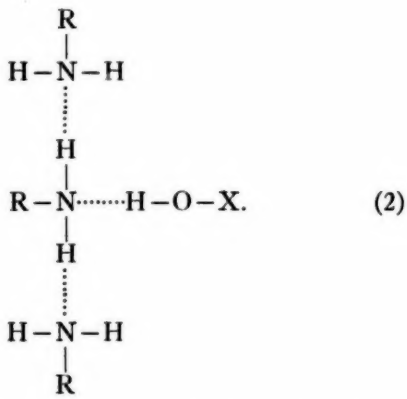
Such a linkage would decrease the effective negative charge on the nitrogen and thus

[11] T. S. Moore and T. F. Winmill, J. Am. Chem. Soc. 91, 1373 (1907).

[12] J. T. Edsall, J. Chem. Phys. 5, 225 (1937).

[13] The author has obtained data, soon to be published, which shows that the hydrogen bonds in liquid aniline are very much weaker than those in liquid alcohol; the shift in the NH_2 absorption due to this bonding is approximately one-fourth that of the hydroxyl band. Similarly, the data shows that the association of aniline with an oxygenated solvent like ether, although it apparently occurs to some extent, is very much weaker than the association of alcohol with the same solvent. Huggins (J. Organic Chem. 1, 407 (1936)) has emphasized the improbability of strong hydrogen bonds being formed through an amine hydrogen.

increase the acceptor power of the amine hydrogens, making possible complexes of the type,



(2)

It is not unlikely that (1) and (2), with perhaps even more complex forms, exist in dynamical equilibrium, and this may explain why the OD band is broad and apparently double when the solvent is a primary amine. A similar interpretation would hold for the secondary amines.

By means of Fig. 3, E, F and G, it is possible to compare the primary, secondary and tertiary forms of butylamine. Although the differences are not great, the maximum of absorption of the hydroxyl band appears at longer wave-lengths for the tertiary than for the secondary, and at longer wave-lengths for the secondary than for the primary. When the solvent was pyridine[14] the OD band appeared at the same position as the associational band of liquid CH_3OD. To make sure that the shift observed here was not caused by association between the alcohol molecules rather than by association of the alcohol with the pyridine, concentrations as low as $0.1M$ were obtained. At this concentration, even in benzene, the association between the alcohol molecules is almost completely broken down. At $0.1M$ the band appeared at the same position as for one M, and the author is inclined to think that the shift here is due almost entirely to association between the solute and the solvent. In determining the effects of hydrogen bonding between unlike molecules, it is, of course, necessary to compare the solution band with the monomolecular band rather than with the liquid band which has already been affected by association. Also it is imperative that the solution be sufficiently dilute so that

[14] J. Errera and H. Sack (Trans. Faraday Soc. **34**, 728 (1938)) have recently repeated the author's measurements on mixtures of ordinary alcohol with dioxan and with acetone, and in addition have obtained data for CH_3OH in pyridine, which agree with the results reported here for CH_3OD in pyridine.

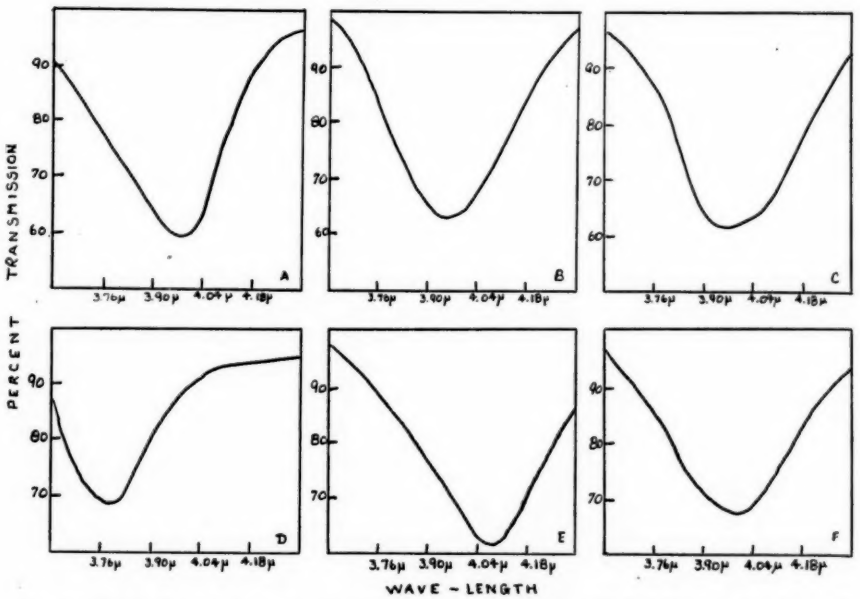


FIG. 4. Effects of solvent on the spectrum of D_2O. A. Pure liquid. Solutions ($1M$, $t=0.006$ cm) in: B. Pyridine; C. Nicotine; D. Methyl cyanide; E. Piperidine; F. Picoline.

association between the solute and solvent will predominate over the association between the molecules of the solute. It may be the failure to take these things into consideration which caused Edsall[12] to conclude from his measurements that there is little interaction between water and the amines. The effects of piperidine and of quinoline on the hydroxyl band are especially pronounced. For solutions of CH_3OD in these the shifted band appears at appreciably longer wave-lengths than does the pure liquid band. The effects of α-picoline on the band are about the same as those of pyridine. In nicotine solution the OD band appears double, a fact which may indicate that the two nitrogen atoms in the nicotine molecule have different effective charges.

In Fig. 4 are shown the effects of some of these solvents on the D_2O spectrum. Here the corresponding monomolecular band is not shown. To determine the shift due to association one should compare the position of the band of the solution with that of the D_2O vapor band, which appears at 5.59μ.[15] It will be observed that the effects of the different solvents on the D_2O band are approximately the same as those on the CH_3OD band.

TABLE I.

CH_3OD SOLUTIONS

Solvent	Position of OD band		Shift from monomolecular band in benzene solution	
	μ	cm^{-1}	$\Delta\mu$	$\Delta\nu$
Benzene	3.73	2681		
Bromobenzene	3.73	2681	0	0
Pure liquid	4.01	2494	0.28	187
Nitrobenzene	3.77	2653	.04	28
o-Nitrotoluene	3.80	2632	.07	49
Ethyl acetate	3.85	2597	.12	84
Amyl acetate	3.86	2591	.13	90
n-Butyraldehyde	3.90	2564	.17	117
Benzaldehyde	3.85	2597	.12	84
Methyl ethyl ketone	3.84	2604	.11	77
Acetone	3.87	2584	.14	97
Dioxan	3.87	2584	.14	97
Diethyl ether	3.92	2551	.19	130
iso-Propyl ether	3.91	2558	.18	123
n-Butyl ether	3.89	2571	.16	110
Methyl cyanide	3.82	2618	.09	63
Benzyl cyanide	3.84	2604	.11	77
Monoamylamine	3.95	2532	.22	149
Di-*n*-propylamine	4.03	2481	.30	200
Monobutylamine	3.98	2513	.25	168
Di-*n*-butylamine	4.04	2475	.31	206
Tributylamine	4.06	2463	.33	218
Pyridine	4.00	2500	.27	181
Piperidine	4.10	2439	.37	242
Quinoline	4.12	2427	.39	254
a-Picoline	4.02	2488	.29	193
Nicotine	4.02	2488	.29	193

D_2O SOLUTIONS

Solvent	Position of OD band		Shift from monomolecular band of vapor state	
	μ	cm^{-1}	$\Delta\mu$	$\Delta\nu$
Vapor*	3.59	2784		
Liquid	3.99	2507	0.40	277
Pyridine	3.97	2519	.38	265
Nicotine	3.99	2507	.40	277
Methyl cyanide	3.78	2646	.19	138
Piperidine	4.09	2469	.50	315
a-Picoline	3.99	2507	.40	277

* From E. F. Barker and W. W. Slater, J. Chem. Phys. **2**, 660 (1935).

Tabular comparison of data

Table I has been arranged to make convenient a comparison of the shifts of the OD band produced by the different solvents. Because of the broadness and complexity of the band in many of the solutions it was not possible to decide accurately the position of its center. It is not probable, however, that the error in any case exceeds 0.025μ.

DISCUSSION

The modern definition of a base as a proton acceptor[16] carries with it the meaning that the basicity of a substance is determined by its tendency to acquire protons. This new conception has added a great group of organic liquids to the substances formerly considered as bases and has considerably complicated the problem of determining basicities.[17] Obviously the measurement of tendency to acquire protons is not always synonymous with measurement of hydroxyl ion concentration. There is no apparent reason why the modern definitions of acids as proton donors and of bases as proton acceptors should not include all substances which participate in intermolecular hydrogen bond formation. The substance which provides the proton in hydrogen bonding can be thought of as an acid and the substance which shares this proton, as

[15] E. F. Barker and W. W. Slater, J. Chem. Phys. **2**, 660 (1935).

[16] K. W. Sherk, J. Chem. Educ. **13**, 358 (1936); J. N. Bronsted, Chem. Rev. **5**, 23 (1928).

[17] Choh-hao Li and T. D. Stewart, J. Am. Chem. Soc. **59**, 2596 (1937).

a base. The process of ionization of an acid by a basic solvent may be thought of as resulting from the formation of unsymmetrical hydrogen bridges between the acid molecules and the molecules of the solvent, the bonding so reducing the force constant of the acid molecule that it is easily dissociated by molecular motions. Thus hydrogen bond formation would precede ionization.

Assuming that the magnitude of the shift in the hydroxyl band is determined by the magnitude of the attraction of the base for the proton, or deuteron, we have here a direct and convenient method of comparing the intrinsic strengths of bases. It is interesting to note that this method of comparison gives the relative basicities of the amines in the order, tertiary >secondary>primary.

It was the purpose of the present report to show the wide occurrence of hydrogen bonding between unlike molecules and to demonstrate a new and seemingly desirable method of comparing the proton-attracting powers of different liquids. Consequently only a few liquids from each of several different classes were studied. It should prove worth while to extend these studies to include more liquids of a given class and to make a general classification of all the commonly used solvents on the basis of the shift which they will produce in the OH or OD band of a given hydroxyl compound. From the results given here it is possible to predict the association between these solvents and other proton donor or acidic type solutes, as is shown in the following paper on solutions of HCl and as will be shown in a later report on solutions of chloroform in some of these solvents.

The writer wishes to express his thanks to Dr. H. H. Nielsen, in whose laboratory this work was done, for his constant interest, and to Dr. Alpheus W. Smith, Head of the Department of Physics, for his interest and support. The author is also indebted to Dr. Edwin Lassettre, of the Department of Chemistry, for his helpful discussion of the data.

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The Infra-Red Absorption of HCl in Solution

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The fundamental HCl vibrational band has been observed for solutions of HCl in nitrobenzene, *o*-nitrotoluene, ethyl acetate, di-ethyl ether, iso-propyl ether, *n*-butyl ether, and dioxan. The band is shifted appreciably to lower frequencies in all of these solvents. The shifts are too great to be attributed wholly to the dielectric constants of the solvents; they are interpreted as being caused primarily by hydrogen bonding between the HCl and the solvent.

THE method used in the preceding paper to study the association between hydroxyl compounds and certain liquids has been employed in the present study to investigate HCl solutions. A preliminary report of the results has been given.[1]

Plyler and Williams[2] have observed the HCl fundamental in the infra-red for a solution of HCl in benzene and have reported the absence of the band for aqueous solutions of HCl. They found that the band which occurs at 3.46μ in gaseous HCl is only slightly shifted to the longer wave-lengths in the benzene solution. Later Williams[3] showed that the shift is much more pronounced for HCl solutions in nitrobenzene and *m*-nitrotoluene. West and Arthur,[4] who have observed the Raman spectra of HCl in a number

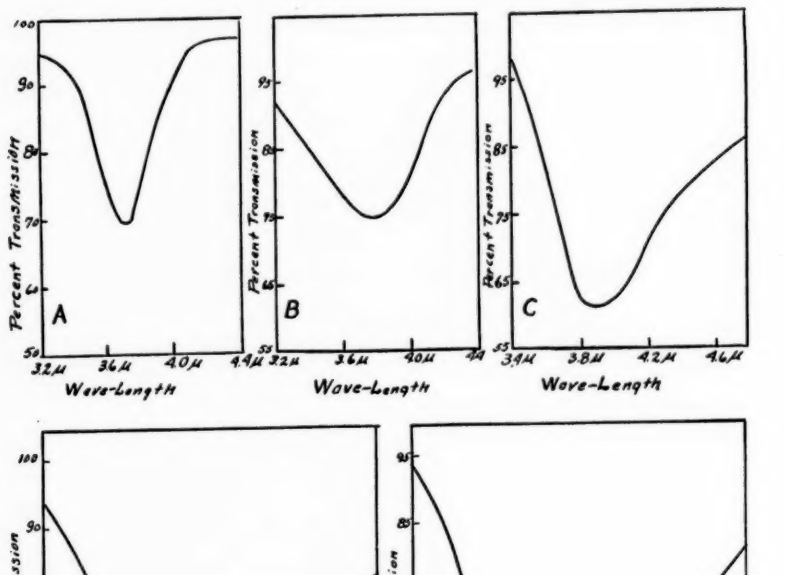
* Present address: Mary Hardin-Baylor College, Belton, Texas.

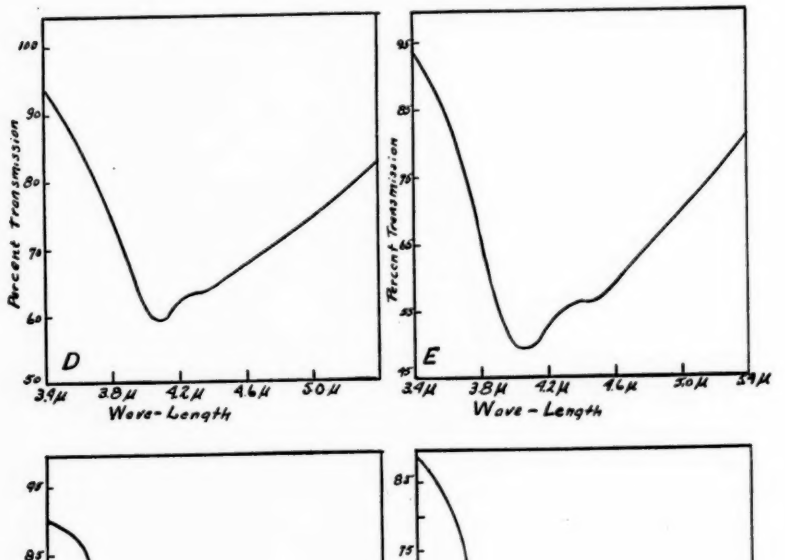
[1] W. Gordy and P. C. Martin, Phys. Rev. **52**, 1075 (1937).

[2] E. K. Plyler and D. Williams, Phys. Rev. **49**, 215 (1936).

[3] D. Williams, Phys. Rev. **50**, 719 (1936).

[4] W. West and P. Arthur, J. Chem. Phys. **2**, 215 (1934); **5**, 10 (1937); M. Walkenstein and J. K. Syrkin, Nature **139**, 288 (1937).





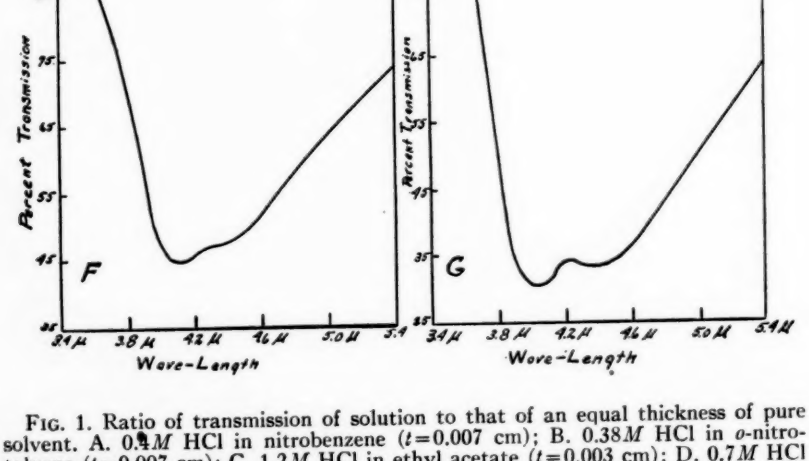


FIG. 1. Ratio of transmission of solution to that of an equal thickness of pure solvent. A. 0.4M HCl in nitrobenzene (t=0.007 cm); B. 0.38M HCl in o-nitrotoluene (t=0.007 cm); C. 1.2M HCl in ethyl acetate (t=0.003 cm); D. 0.7M HCl in n-butyl ether (t=0.005 cm); E. 0.82M HCl in di-ethyl ether (t=0.005 cm); F. 0.8M HCl in iso-propyl ether (t=0.005 cm); G. 1.1M HCl in dioxan (t=0.004 cm).

of nonconducting solutions, found that the position of the HCl band depended upon the dipole moment of these solvents. All previous attempts to observe the characteristic absorption of HCl in solution in so-called active solvents like ether have failed, both in the Raman[4] and infra-red spectra,[5] a fact which has led many to conclude that HCl in solvents of this type is almost, if not completely, ionized. It is now generally believed that the ionization of an acid by a given solvent is more a result of the tendency of the acid proton to unite with some atom of the solvent through a chemical bond than of the weakening of the binding force of the acid by electrostatic forces caused by the dipole moment of the solvent. West and Arthur,[4] for example, have shown by their studies in the Raman spectra that the dissociation of HCl by purely dipole interaction would require a solvent of greater dielectric constant than any yet found. It is well known that HCl in many solvents of low dielectric constant forms conducting solutions, while its solutions in many solvents of much higher dielectric constant are practically nonconducting. It was proposed in the foregoing paper that the dissociation of an acid by a given solvent may be preceded by intermolecular hydrogen bond formation between the acid and the solvent molecules. If the hydrogen bonds are extremely unsymmetrical—the solvent having the greater attraction for the proton—the acid bond may be so weakened that at ordinary temperatures the acid would be completely dissociated by molecular motion. If, on the other hand, the attraction of the solvent for the acid proton is sufficient to form hydrogen bonds but not enough to make the acid bond easily disrupted by molecular motion, the HCl vibrational band should still be observable in the infra-red, although it would certainly be shifted to the longer wave-lengths because of the association. From the previously observed effects of hydrogen bonding on the hydroxyl band of alcohol,[6] one would expect the shifts in the HCl band due to hydrogen bonding to be, in general, much greater than any shifts due solely to the dielectric constant of the solvent.[4]

[5] W. West and R. T. Edwards, J. Chem. Phys. **5**, 14 (1937).

[6] See preceding paper on spectroscopic comparison of proton-attracting properties.

Discussion of Results

The solvents used were nitrobenzene, *o*-nitrotoluene, ethyl acetate, di-ethyl ether, iso-propyl ether, *n*-butyl ether and dioxan. For all the solutions absorption was recorded, which the authors believe is due to HCl. The results are shown in Figs. 1 and 2. The curves were obtained by the instrument discussed in the foregoing paper.

The curve for the HCl-nitrobenzene solution is essentially the same as that previously reported by Williams.[3] It is repeated here for purposes of

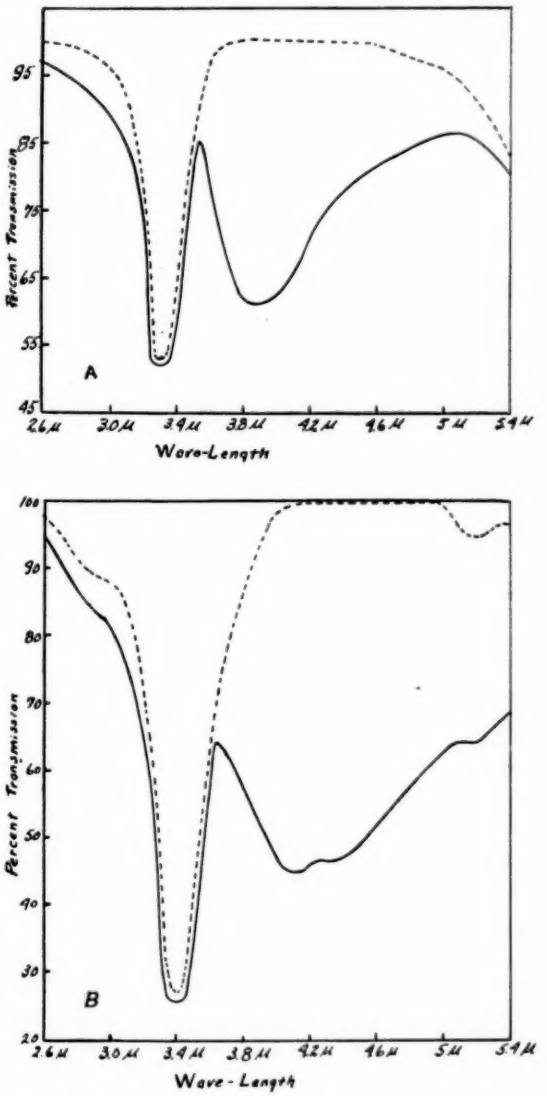


FIG. 2. Percentage transmission of pure solvent and HCl solutions. A. Ethyl acetate (broken line) and 1.2 *M* (t=0.003 cm), solution (solid line); B. iso-Propyl ether (broken line) and 0.8 *M* (t=0.005 cm), solution (solid line).

TABLE I.

SOLVENT	POSITION OF HCl BAND		SHIFT FROM POSITION OF GAS BAND	
	μ	cm^{-1}	$\Delta\mu$	$\Delta\nu$
Gas*	3.46	2890		
Nitrobenzene	3.70	2703	.24	187
o-Nitrotoluene	3.78	2646	.32	244
Ethyl acetate	3.88	2577	.42	313
Di-ethyl ether	4.08	2451	.62	439
iso-Propyl ether	4.12	2427	.66	463
n-Butyl ether	4.08	2451	.62	439
Dioxan	4.05	2469	.59	421

* See H. M. Randall and E. S. Imes, Phys. Rev. **15**, 152 (1920).

comparison. As might be expected, the results obtained for the *o*-nitrotoluene solution are practically the same as those reported by Williams[3] for HCl in *m*-nitrotoluene. In both nitrobenzene and *o*-nitrotoluene solution the HCl band appears at wave-lengths appreciably longer than does the the gaseous HCl band. In consideration of the effects of dielectric constant of the solvent determined by West and Arthur,[4] the shifts to lower frequencies are here too great to be ascribed to dielectric constant alone. The authors are inclined to interpret them as caused primarily by hydrogen bonding between the HCl and the solvent. In the preceding paper evidence is given for very weak hydrogen bonds between these nitro-compounds and alcohol. The greater shift produced by *o*-nitrotoluene over nitrobenzene is probably caused by a greater electron donor power of its bonding oxygens than to its slightly greater dipole moment.

For HCl solutions in ethyl acetate there seems to be no question but that there is complex formation between the solute and solvent. The HCl band appears at 3.88μ, having been shifted 0.42μ, or 313 wave numbers, from the position of the gas band. Since the shift is much too great to be caused by the dipole moment of the solvent, the authors believe it is a result of hydrogen bonding.

In the ether solutions the HCl band is shifted to still lower frequencies and is markedly broadened. A slight rise at about 4.26μ in each of these curves makes the band appear double. At this point the galvanometer deflections were reduced noticeably because of atmospheric CO_2 absorption. Thus it was not possible to ascertain whether the doubling of the band is real or whether it is a falsification. Unfortunately the broadness of the band, together with the experimental difficulty mentioned above, made it impossible to decide where its center occurs. The results do show, however, that there is appreciable absorption in the region 4.0μ to 4.5μ, which may be ascribed to the HCl linked through hydrogen bonds with the solvent.

The curves in Fig. 1 represent the ratio of the transmission of the solution to that of an equal thickness of the pure solvent. Two of the solution curves with the corresponding curves for the pure solvent appear in Fig. 2. These curves make possible a comparison of the intensity of the HCl band with that of the CH band of the solvent.

Table I makes possible a comparison of the approximate shifts which the different solvents produce in the band. From these results it is evident that HCl is not completely ionized in any of these solvents but that the binding force between the H and Cl has been weakened perceptibly by association with the solvent.

The previous attempts to observe the infra-red absorption of HCl in ether solution were made in the region of the first harmonic. It is quite possible that the hydrogen bonding makes the potential energy function so nearly a Hooke's-law function that the first harmonic cannot be detected. In many cases of hydrogen bonding involving a hydroxyl hydrogen the first harmonic of the OH vibrational band is absent.[7] It is interesting that the Raman spectra does not show any lines which can be attributed to HCl in ether solutions. Also, the OH fundamental of a hydroxyl group joined in hydrogen bond formation is very intense in the infra-red, while in the Raman spectra it is either extremely weak or absent entirely.[8] These results suggest that an effect of hydrogen bonding is to make the Raman line inactive.

The writers wish to express their appreciation to Dr. Alpheus W. Smith and to Dr. H. H. Nielsen, whose interest and support made this work possible.

[7] G. E. Hilbert, O. R. Wulf, S. R. Hendricks and U. Liddell, Nature **135**, 147 (1935).
[8] C. S. Venkateswaran, Proc. Ind. Acad. Sci. **7**, 13 (1938).

Grand Partition Functions and So-Called "Thermodynamic Probability"

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The relation due to Boltzmann between entropy and "thermodynamic probability" is enunciated in a precise form. This relation is generalized in such a way that each of the other thermodynamic potentials is related in a similar manner to a "thermodynamic probability," for which a more suitable name is a "partition function."

1. MICRO- AND MACRODESCRIPTIONS OF AN ASSEMBLY

ACCORDING to quantum theory the state of an assembly is completely described by its eigenfunction. To each state there corresponds one eigenfunction and to each eigenfunction one state. The expression "degenerate state of weight Ω" is an abbreviation for a group of Ω states between which we do not care to distinguish. Such a description of the assembly we shall call a microdescription.

It is often, though not always, possible to regard the assembly as consisting of a large number of almost independent systems (molecules, atoms, ions, electrons) and to express each eigenfunction of the assembly as a linear combination of products of the eigenfunctions of all the systems. According to the symmetry restrictions, if any, imposed on the eigenfunctions of the assembly, one then obtains three alternative sets of statistical formulae referred to by the names of Fermi-Dirac, Bose-Einstein and Boltzmann, respectively. These three alternatives, however, arise only when one expresses the eigenfunctions of the assembly in terms of those of the constituent systems. As we shall consistently refer only to the eigenfunctions of the whole assembly, we shall not need to consider these three alternatives separately.

When we describe the equilibrium properties of an assembly by thermodynamic methods, we are not interested in such a precise description as the microdescription, but are content with a more crude large scale description, which we shall call a macrodescription. For example a possible macrodescription of the assembly would be a precise statement of the energy, the volume, the exact chemical composition (and in special cases other quantities all measurable on a large scale) of each homogeneous part or phase. For brevity we shall confine our discussion entirely to assemblies whose macrodescription requires a precise statement of only four quantities. The extension of the argument to more complicated assemblies should be obvious. Initially we shall take the first of these quantities to be the energy, the second to be the volume, the third to be the empirical composition; the nature of the fourth quantity is best indicated by some specific examples.

Example 1. Let us consider a definite quantity of hydrogen (free from deuterium) of given energy and given volume. Then we can complete the description by a statement of what fraction of it is *para*, the remaining fraction being *ortho*.

Example 2. If instead of hydrogen, we have lactic acid we can complete the description by a statement of what fraction is dextro, the remaining fraction being laevo.

Example 3. If the assembly consists of a given quantity of iodine of given energy and volume we can complete the description by a statement of what fraction is in the diatomic form I_2, the remainder being in the monatomic form I.

Example 4. If the assembly consists of a given quantity of tin of given energy and volume, we can complete the description by stating what fraction is white, the remainder being gray.

Example 5. If the assembly consists of a given quantity of carbon dioxide, we may complete the description by stating what fraction is liquid, the remainder being vapor.

In examples 1–3 it is tacitly assumed either that the assembly is homogeneous or, if it consists of two phases, that we are not interested in the relative amounts, these being determined by the other conditions. Another example that might be suggested is an assembly of a given quantity of hydrogen of given energy and volume for which we were interested both in the ratio of *para* to *ortho* and in the ratio of liquid to vapor.

Such an assembly, however, requires five quantities, instead of four, to complete its macrodescription and so lies outside the class which we shall discuss, although the extension of the treatment to such an assembly in fact offers no difficulty.

Having made clear by these examples the nature of the fourth independent variable describing the assembly we shall denote this variable by ξ. It corresponds approximately to the quantity which De Donder[1] and his school call the degree of advancement of a physico-chemical change. It is not a necessary property of ξ that one should be able completely to control its value, provided that its value can in principle be measured by macroexperiments. As an example of a ξ which cannot be controlled we might mention the fraction of molecules in a gaseous assembly which have more than a prescribed amount of energy of a specified kind. Although such a ξ cannot be controlled it can be measured, for example, by observing rates of escape (diffusion) or rates of chemical reaction.

2. Assembly of Given Energy, Volume and Composition

Let us now consider in more detail an assembly of prescribed energy E, prescribed volume V and containing a prescribed number N of units (grams or lb. or moles) of a given substance. Let the number of eigenfunctions of the assembly consistent with the prescribed values of E, V, N and corresponding to a particular value of the parameter ξ be denoted by $\Omega(E, V, N, \xi)$. As long as we are not interested in distinguishing between the states of equal ξ, we can group them together into a degenerate state of weight $\Omega(E, V, N, \xi)$. Then the average properties of the assembly for the prescribed values of E, V, N can be derived statistically by averaging over all degenerate states attaching to each a weight $\Omega(\xi)$.

We now define a quantity $S(E, V, N, \xi)$ by the relation

$$S(E, V, N, \xi) = k \log \Omega(E, V, N, \xi), \quad (2.1)$$

where k is a universal constant, which merely fixes the units in which S is measured. It can then be shown that S has all the properties of the entropy of the assembly in the macrostate defined by E, V, N, ξ. Formula (2.1) is a precise formulation of the well-known relation due to Boltzmann, to whom the name "thermodynamic probability" for $\Omega(E, V, N, \xi)$ is due. This name can be harmless as long as it is realized that "thermodynamic probability" so defined is not a probability in the ordinarily accepted sense of the word. We prefer to call $\Omega(E, V, N, \xi)$ the partition function for given E, V, N, ξ. The reason for our choice of this name will become clearer as we proceed.

We shall show that Boltzmann's relation (2.1) between the entropy and the partition function (or thermodynamic probability) is merely one of a number of relations of a similar type, between other thermodynamic potentials and other partition functions (or thermodynamic probabilities). It should be noted that the entropy is a thermodynamic potential for the variables E, V, N which we have hitherto taken as independent. This is shown by the relation, holding either for constant ξ or for ξ maintained at its equilibrium value,

$$dS = dE/T + PdV/T - \mu dN/T, \quad (2.2)$$

where T denotes absolute temperature, P denotes pressure and μ denotes the partial potential of the given substance.

3. Assembly of Given Temperature, Volume and Composition

We shall now consider an assembly whose volume V and composition N are still prescribed, but instead of prescribing the energy we shall suppose the assembly to be in thermal equilibrium with a large reservoir of prescribed temperature T. Let us now enumerate the eigenfunctions of the assembly for the prescribed values of V and N and for some definite value of ξ; let there be $\Omega_0(\xi)$ such eigenfunctions corresponding to an energy $E_0(\xi)$; $\Omega_1(\xi)$ corresponding to an energy $E_1(\xi)$ and so on. We now define the function $f(T, N, V, \xi)$ by the relation

$$f(T, N, V, \xi) = \Omega_0(\xi) e^{-E_0(\xi)/kT} + \Omega_1(\xi) e^{-E_1(\xi)/kT} + \cdots = \Sigma_r \Omega_r(\xi) e^{-E_r(\xi)/kT}. \quad (3.1)$$

[1] De Donder and P. Van Rysselberghe, *Affinity* (Stanford University Press, 1936), p. 2.

The average properties of the assembly for the prescribed values of T, V, N can then be obtained by averaging over all values of ξ assigning to each a weight $f(T, V, N, \xi)$. This useful function $f(T, V, N, \xi)$ is well known under the name partition function[2] (or *zustandsumme*).

As we proceed it will become clear that a precise name would be the partition function for given T, V, N, ξ. We now define a function $F(T, V, N, \xi)$ by the relation

$$-F(T, V, N, \xi)/T = k \log f(T, V, N, \xi). \quad (3.2)$$

It can then be shown that F has all the properties of the free energy of the assembly in the macrostate of given T, V, N, ξ. We also note, according to the relation, holding either for constant ξ or for ξ maintained at its equilibrium value,

$$d(-F/T) = EdT/T^2 + PdV/T - \mu dN/T, \quad (3.3)$$

that $-F/T$ (or alternatively F) is a thermodynamic potential for the independent variables T, V, N.

4. Assembly of Given Temperature, Volume and Partial Potential

We shall now consider an assembly of prescribed volume and temperature separated by an ideal membrane, permeable to the substance of which it is composed, from a large reservoir at the same temperature and containing this substance in a well-defined macrostate. Under these conditions the assembly has a prescribed value of μ, determined by the reservoir of the substance, instead of a prescribed value of N. We now consider all possible eigenfunctions for the specified value of V, but unspecified values of E and of N, which correspond to a definite value of ξ, and we construct the function $\Xi(T, V, \mu, \xi)$ defined by

$$\Xi(T, V, \mu, \xi) = \Sigma_r \Sigma_t \Omega_{rt}(\xi) e^{-E_r/kT} e^{N_t \mu/kT}, \quad (4.1)$$

where Ω_{rt} denotes the number of states of energy E_r and content N_t corresponding to the relevant value of ξ and the double summation extends over all states with the prescribed volume V corresponding to the relevant value of ξ. We can now derive all the equilibrium properties of the assembly for the prescribed values of T, V, μ by averaging over all values of ξ attaching to each the weight $\Xi(T, V, \mu, \xi)$. In this sense $\Xi(T, V, \mu, \xi)$ is the thermodynamic probability of the relevant ξ for the prescribed values of T, V, μ. It can further be shown that

$$PV/T = k \log \Xi, \quad (4.2)$$

and according to the relation, holding either for constant ξ or for ξ maintained at its equilibrium value,

$$d\left(\frac{PV}{T}\right) = \frac{(TS - PV)dT}{T^2} + \frac{P}{T}dV + \frac{N}{T}d\mu, \quad (4.3)$$

we see that PV/T (or alternatively PV) is a thermodynamic potential for the independent variables T, V, μ.

The usefulness of Ξ has been pointed out recently by Fowler,[3] who proposes the name grand partition function because of its close connection with Gibbs' grand ensemble. An alternative suitable name would be partition function for the independent variables T, V, μ, ξ.

5. Further Generalization of Partition Functions or Thermodynamic Probabilities

None of the relations mentioned hitherto is by any means new. Those of Sections 2 and 3 will be familiar to all readers. Those of Section 4 are based on the recent article by Fowler.[3] We have therefore considered it superfluous to give derivations of these relations, but have endeavored to cite them in such a manner as to emphasize the complete analogy between the three sets of relations holding for the three sets of independent variables. This analogy appears to have been only incompletely realized; otherwise the expression thermodynamic probability would not have been applied only to $\Omega(E, V, N, \xi)$ to the exclusion of $f(T, V, N, \xi)$ and $\Xi(T, V, \mu, \xi)$. When the analogy is completely appreciated, it becomes almost evident that there should be other analogous relations for other sets of independent variables. In the following sections we shall

[2] R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, 1936).

[3] R. H. Fowler, Proc. Camb. Phil. Soc. **34**, 382 (1938).

enunciate these new relations. We shall not give derivations as these would be exactly parallel to those for the independent variables T, V, N, ξ. The most powerful method of deriving them *a priori* is certainly the method of expressing the number of accessible states, subject to the prescribed values of the independent variables, as contour integrals and applying the method of steepest descents. The procedure will be obvious to the reader who is already familiar with the previous use of this method by Darwin and Fowler.[2] Alternatively the correctness of the relations, which we shall enumerate, can be verified from the fact that they lead to consequences thermodynamically equivalent to those of the previous sections.

6. Assembly of Given Temperature, Pressure and Content

We now consider an assembly of prescribed content surrounded by a temperature bath and enclosed by a cylinder with a piston subjected to a prescribed pressure P. We now construct the double sum $W(T, P, N, \xi)$ defined by

$$W(T, P, N, \xi)=\Sigma_r\Sigma_s\Omega_{rs}(\xi)e^{-E_r/kT}e^{-PV_s/kT}, \quad (6.1)$$

where Ω_{rs} denotes the number of states of energy E_r and volume V_s corresponding to the relevant value of ξ and the double summation extends over all states with the prescribed content N corresponding to the relevant value of ξ. We can now derive all the equilibrium properties of the assembly for the prescribed values of T, P, N by averaging over all values of ξ attaching to each a weight equal to $W(T, P, N, \xi)$, this expression being the partition function for the independent variables T, P, N, ξ. It can further be verified that the Gibbs function $G=F+PV$ is related to $W(T, P, N, \xi)$ by

$$-G/T=k \log W(T, P, N, \xi), \quad (6.2)$$

and according to the relation, holding either for constant ξ or for ξ maintained at its equilibrium value,

$$d(-G/T)=HdT/T^2-VdP/T-\mu dN/T, \quad (6.3)$$

we see that $-G/T$ (or alternatively G) is a thermodynamic potential for the independent variables T, P, N. In formula (6.3) we have used H to denote the total heat (or heat content) equal to $E+PV$.

7. Assembly of Given Temperature, Pressure, and Partial Potential

To conclude we choose as independent variables the temperature T, pressure P and partial potential μ. An illustrative example is a small crystal surrounded by a large quantity of its own vapor mixed with some inert gas; the gaseous phase is not considered as part of the assembly. Such an assembly may be described as *completely open*. We now construct the triple sum

$$W(T, P, \mu, \xi)=\Sigma_r\Sigma_s\Sigma_t\Omega_{rst}e^{-E_r/kT} \times e^{-PV_s/kT}e^{N_t\mu/kT}, \quad (7.1)$$

where Ω_{rst} denotes the number of states of energy E_r, volume V_s and content N_t corresponding to the relevant value of ξ and the triple summation extends over all sets of values of E_r, V_s, N_t corresponding to the relevant value of ξ. We can now derive all the equilibrium properties of the assembly for the prescribed values of T, P, μ by averaging over all values of ξ attaching to each a weight equal to $W(T, P, \mu, \xi)$, this expression being the partition function for the independent variables T, P, μ, ξ. It can further be verified that $\log W$ is vanishingly small, and according to the relation, holding either for constant ξ or for ξ maintained at its equilibrium value,

$$0=SdT-VdP+Nd\mu, \quad (7.2)$$

we see that the thermodynamic potential for the independent variables T, P, μ is identically equal to zero.

8. Recapitulation

We can now summarize the content of the several preceding sections. For each of the selected sets of three independent variables, other than ξ, a different kind of weighting factor w has to be attached to the microstates. The sum $W(\xi)$ of these weighting factors w for all microstates consistent with the prescribed values of the three chosen independent variables other than ξ and corresponding to a definite value of ξ may be called the partition function for the prescribed

TABLE I.

INDEPENDENT VARIABLES	WEIGHTING FACTOR FOR EACH INDEPENDENT MICROSTATE OF ASSEMBLY w	USUAL NAME FOR THE PARTITION FUNCTIONS $W(\xi)=\Sigma w$	THERMODYNAMIC POTENTIAL EQUAL TO $k \log W(\xi)$
E, V, N, ξ	1	Weight	S
T, V, N, ξ	$e^{-E/kT}$	Partition function	$-F/T$
T, V, μ, ξ	$e^{-(E-N\mu)/kT}$	Grand partition function	PV/T
T, P, N, ξ	$e^{-(E+PV)/kT}$	—	$-G/T$
T, P, μ, ξ	$e^{-(E+PV-N\mu)/kT}$	—	0

values of ξ and the other three independent variables. Furthermore $k \log W(\xi)$ is in each case equal to a thermodynamic potential for the selected set of three independent variables other than ξ. These relationships are made clear in the Table I. The remaining sets of independent variables E, ξ together with V, μ or P, N or P, μ are of little physical interest because of the difficulty of prescribing a fixed value for the energy of an assembly that is not completely closed.

9. TERMINOLOGY

In conclusion we would suggest the following terminology, which seems reasonably logical and does not depart too seriously from current practice. All the functions $W(\xi)=\Sigma w$ are partition functions. The term *partition function* thus becomes the statistical analog of a *thermodynamic potential.* Whenever there is any possibility of confusion between the several partition functions, one should specify the independent variables, e.g., partition function for the variables T, P, N. When there is no risk of ambiguity, the term partition function may also be used in its original sense to denote the partition function for the variables T, V, N. Alternatively this can be called the *ordinary partition function.* The partition function for the variables E, V, N is most simply called the *weight.* The three remaining partition functions can be contrasted with the ordinary partition function by calling them *generalized partition functions* or alternatively *grand partition functions.*

To any readers who prefer to use the name thermodynamic probability instead of partition function, we would point out that there is a different thermodynamic probability for each of the five sets of independent variables.

I have great pleasure in thanking Professor R. H. Fowler for the interest he has taken in this paper and I have his permission to say that he agrees with my views on terminology.

The Free Energy of Hydration of Gaseous Ions, and the Absolute Potential of the Normal Calomel Electrode

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The free energies of hydration of the alkali and halide ions are found to agree reasonably well with the simple expression of Born ($-\Delta F=(1-1/D)Ne^2/2r_e$) for solution of charged spheres in a dielectric medium, provided the crystal radii are suitably modified so as to correspond to the radii of the cavities in the dielectric medium. The results show that the dielectric constant of water remains large even in the intense field next to the ion. The entropies of hydration are also found to be consistent with these radii. Because of the simplicity of this calculation, the resulting free energies of solution of individual ions are considered to be *a priori* the most probable and are used to calculate a value of -0.50 volt for the absolute potential of the calomel half-cell.

SEVERAL discussions of the energy of hydration of gaseous ions have been published recently.[1-3] In these the simple Born expression ($-\Delta F=Ne^2/2r_e[1-1/D]$) is considered, but declared to be unsatisfactory in some important respects. In most cases modifications were introduced which complicated the treatment and increased the opportunities for adjustment, after which satisfactory agreement with experiment was obtained. The purpose of the present communication is to point out that the simple Born equation alone gives satisfactory results, indicating that refinements are for the present unnecessary. Furthermore, since such a simple treatment suffices, it is likely that the energies of hydration for single ions thus obtained may have some significance, and so they are employed to calculate the absolute potential of the calomel half-cell.

The heats of hydration of pairs of gas ions were obtained from the crystal energies of Huggins[4] and corrected to 298.1°K, and the heats of solution were from Bichowsky and Rossini.[5]

$$M^+(g)+X^-(g)=MX(s) \qquad \Delta H=-U$$
$$MX(s)=M^+(aq)+X^-(aq) \qquad \Delta H=L$$

$$M^+(g)+X^-(g)=M^+(aq)+X^-(aq); \quad \Delta H=L-U.$$

The entropies of gas ions were calculated from the Sackur equation and corrected to one mole per liter concentrations while the values for aqueous ions were taken from the recent summary of Latimer, Pitzer and Smith.[6]

These data were then combined to give the free energies of hydration for the twenty pairs of ions comprising the alkali halide series. Table I contains these values together with the differences between iodide and each of the other halide ions, computed from the data for each metal; also the differences for the metals computed for each halide. These results show the data to be consistent to within a few kcal., which is also the magnitude estimated for their absolute accuracy.

In fitting the Born expression to these data three arbitrary constants must be introduced. First comes the ever present problem of dividing the free energy of hydration, known only for ion pairs, between the two ions of the pair. Once a single absolute value is specified all others are determined. The other two constants arise from the fact that the well-known crystal radii of Pauling[7] cannot be expected to be directly applicable in the Born expression. Here r_e is the radius of the cavity in the dielectric medium and is closely related to the distance from the center of the ion to the center of the nearest water dipoles. Since the negative ions will have the hydrogens of the surrounding water directed in, their effective radii will be but slightly larger

[1] T. J. Webb, J. Am. Chem. Soc. **48**, 2589 (1926).
[2] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933).
[3] Andr. Voet, Trans. Faraday Soc. **32**, 1301 (1936).
[4] M. Huggins, J. Chem. Phys. **5**, 143 (1937).
[5] F. R. Bichowsky and F. D. Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).
[6] W. M. Latimer, K. S. Pitzer and W. V. Smith, J. Am. Chem. Soc. **60**, 1829 (1938).
[7] L. Pauling, J. Am. Chem. Soc. **49**, 765 (1927).

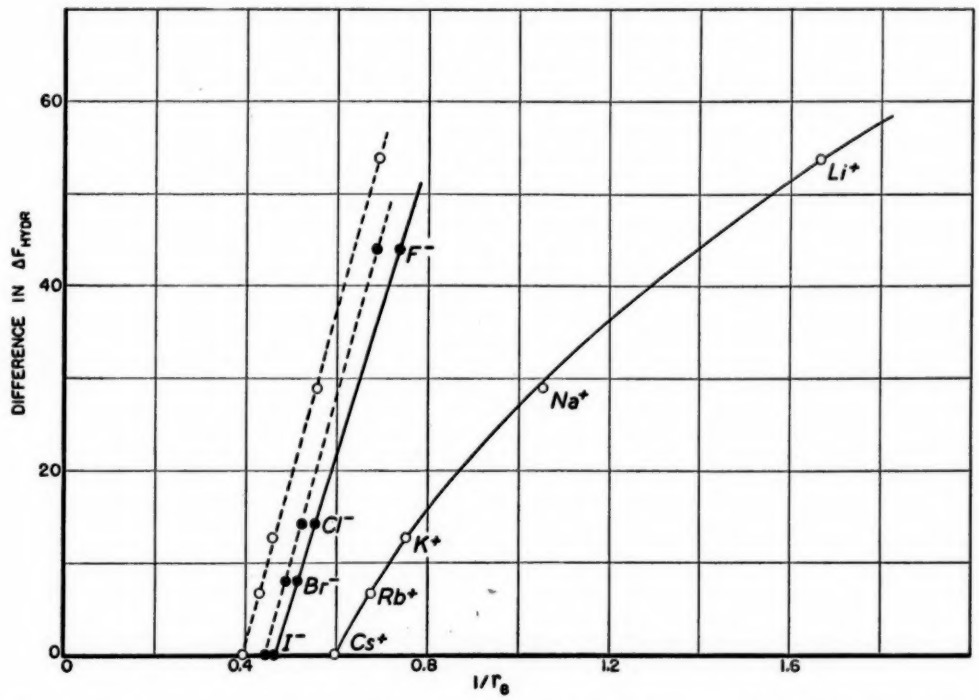

FIG. 1. Differences in free energy of hydration in gaseous ions. Solid curves for crystal radii, dotted for corrected radii.

than the ordinary crystal radii. On the other hand, the positive ions will have the water hydrogens directed out and as a result their effective radii may be considerably larger.

Figure 1 shows the effect of these radii corrections. The differences in free energy of hydration of the negative ions from Table I are first plotted against the crystal radii (solid curve) and a good straight line is obtained. However, it is found that the best fit to the Born expression can be obtained by adding 0.1A to these radii (dotted curve). The similar plot for the positive ions with the crystal radii shows considerable curvature, but upon adding 0.85A to all the radii, a straight line is obtained which, moreover, shows the same slope as the line for the negative ions. Then dividing up the sum of hydration energies for say, cesium and iodide ions so that both positive and negative ions fall on the same curve we obtain Fig. 2, where the line is now the theoretical curve given by the Born equation with the ordinary dielectric constant of water.

TABLE I. *Negative free energies of hydration of pairs of alkali halide gas ions.*

	F^-	$\Delta F_{I^-}-\Delta F_{F^-}$	Cl^-	$\Delta F_{I^-}-\Delta F_{Cl^-}$	Br^-	$\Delta F_{I^-}-\Delta F_{Br^-}$	I^-	MEAN DIFF.
Li^+	229.2	46.8	198.7	16.3	191.5	9.1	182.4	0
$\Delta F_{Cs^+}-\Delta F_{Li^+}$	54.5		55.9		53.3		51.7	53.8±1.4
Na^+	202.6	43.6	173.4	14.4	167.1	8.1	159.0	0
$\Delta F_{Cs^+}-\Delta F_{Na^+}$	27.9		30.6		28.9		28.3	28.9±0.9
K^+	186.3	43.4	157.1	14.2	150.7	7.8	142.9	0
$\Delta F_{Cs^+}-\Delta F_{K^+}$	11.6		14.3		12.5		12.2	12.7±0.9
Rb^+	179.1	41.5	151.5	13.9	145.0	7.4	137.6	0
$\Delta F_{Cs^+}-\Delta F_{Rb^+}$	4.4		8.7		6.8		6.9	6.7±1.1
Cs^+	174.7	44.0	142.8	12.1	138.2	7.5	130.7	0
	0		0		0		0	0
Mean Diff.		43.9 ±1.2		14.2 ±0.9		8.0 ±0.4		0

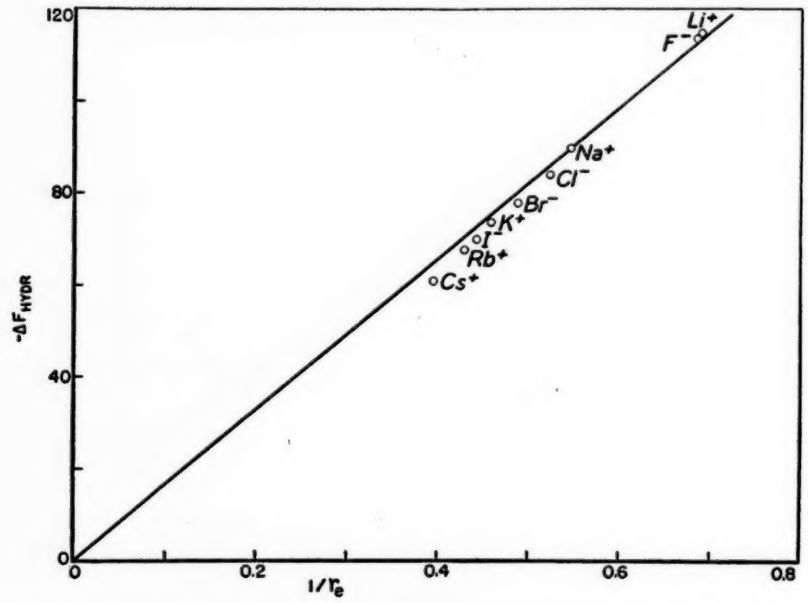

FIG. 2. Free energy of hydration of ions. Straight line represents the Born equation.

Considering that an admittedly over simplified theoretical expression has been used, and that only three arbitrary constants were evaluated while nine experimental data were used (five cations and four anions), the fit in Fig. 2 is to be regarded as quite satisfactory. It should be emphasized that the form of the Born equation is such that the exact value of the dielectric constant is of little significance so long as it remains large compared to unity. The present results show that even in the intense fields next to the ion, the effective dielectric constant of water is fairly high as has been suggested previously.[8, 8a] On the other hand, it is not pretended that the dielectric constant retains its macroscopic value under these conditions.

The foregoing simple assumptions give surprisingly satisfactory results with polyvalent ions; but because of the greater uncertainties in these cases, they will be omitted from the present discussion.

A further test on the above treatment can be made by considering the temperature coefficient of the free energy of hydration, i.e., the entropy of hydration of gas ions. The theoretical expression becomes

$$\Delta S = -\frac{d\Delta F}{dT} = \frac{Ne^2}{2r_e}\frac{1}{D^2}\frac{dD}{dT}.$$

Since this equation is sensitive to small changes in the dielectric constant and its temperature derivative, we cannot expect quantitative agreement; however, we may expect that the entropies of hydration for both positive and negative ions should fall on a single smooth curve.

Using the same effective radii as in the free energy calculations, one still has to divide up the entropy of hydration for a pair of ions between the positive and negative ions. When this is done Fig. 3 is obtained which shows that the positive and negative ions do fall on approximately the same curve when our effective radii are used. The calculation is, of course, essentially that given previously by Latimer.[9]

Since the absolute entropies of the gas ions are known, the absolute entropies of the aqueous ions can now be calculated. The value obtained for chloride ion is 15 cal. per deg. mole which may be compared with the results of Eastman and Young[10] who obtain as a provisional value

[8] W. M. Latimer and C. Kasper, J. Am. Chem. Soc. **51**, 2293 (1929).

[8a] W. J. Dunning and W. J. Shutt, Trans. Faraday Soc. **34**, 467 (1938).

[9] W. M. Latimer, Chem. Rev. **18**, 349 (1936).

[10] M. B. Young, Thesis, University of California, 1935.

18.1 cal. per deg. mole. This agreement is probably as good as can be expected.

Table II contains the data of Fig. 2 and 3 together with the heats of hydration and the absolute ion entropies.

Because of the simplicity and good agreement found above, these values of the free energies of hydration of single ions can be considered to be, *a priori*, the most probable, although by no means conclusively proved. Consequently it seemed worth while to calculate a value for the absolute potential of the normal calomel cell for comparison with experimental values.

The free energy of the calomel half-cell reaction is the sum of the following:

(1) $Na^+(g)=Na^+(aq)$	$\Delta F_{Hydr}=-89.7$
(2) $Na(g)=Na^+(g)+E^-(g)$	$\Delta F = 118.1$
(3) $Na(s)=Na(g)$	$\Delta F = 18.7$
(4) $Hg+Na^+(aq)+Cl^-(aq)=HgCl+Na(s)$	$\Delta F = 68.76$
(5) $E^-(g)=E^-$(in Hg)	$\Delta F=-104.5$
$Hg+Cl^-(aq)=HgCl+E^-$ (in Hg);	$\Delta F = 11.4$ kcal.
	$E_{abs}=-0.495$ volt

Equation (2) is from the table of ionization potentials by Herzberg,[11] Eq. (3) gives the free energy of sublimation and is from the data of Kelley,[12] Eq. (5) is the photoelectric effect in mercury and was determined by Kazda.[13] The value of -0.495 volt for the absolute potential of the normal calomel electrode is in reasonable agreement with the old value of -0.56 obtained from the dropping mercury electrode. The more recent determinations by Billitzer[14] and Garrison[15] differ from ours by some 8 kcal.

We may conclude, as did Baur[16] that the old value of -0.56 volt is our best available experimental value of the absolute potential of the calomel half-cell.

TABLE II. *Thermodynamic properties of single alkali and halide ions.*

	r_e	$-\Delta F°$ HYDR. (kcal.)	$-\Delta S°$ HYDR. (cal./deg.)	$-\Delta H°$ HYDR. (kcal.)	$S°$ ABSOLUTE (cal./deg.)
Li^+	1.45	114.6	22	121.2	3
Na^+	1.80	89.7	17	94.6	12
K^+	2.18	73.5	8	75.8	23
Rb^+	2.33	67.5	6	69.2	27
Cs^+	2.54	60.8	4	62.0	30
F^-	1.46	113.9	29	122.6	− 1
Cl^-	1.91	84.2	15	88.7	+15
Br^-	2.05	78.0	12	81.4	21
I^-	2.26	70.0	7	72.1	27

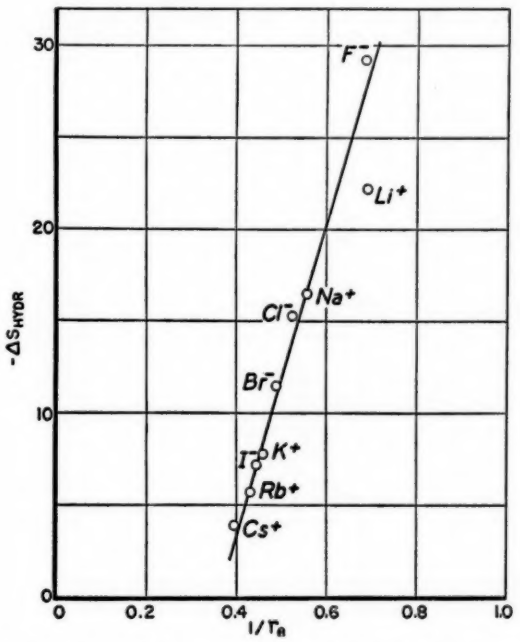

FIG. 3. Entropy of hydration of alkali and halide ions.

[11] G. Herzberg, *Atomic Structure and Atomic Spectra* (Prentice-Hall, 1937).

[12] K. K. Kelley, "Contribution to the Data on Theoretical Metallurgy," Bull. 383, Bureau of Mines (1935).
[13] C. B. Kazda, Phys. Rev. **26**, 643 (1925).
[14] J. Billitzer, Zeits. f. physik. Chemie **48**, 513 (1904).
[15] A. Garrison, J. Am. Chem. Soc. **45**, 37 (1923).
[16] E. Baur, Zeits. Electrochem. **38**, 665 (1932).

The Ignition of Gases by Local Sources

II. Ellipsoid Sources

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(Received November 7, 1938)

The theory of the ignition of gases previously given for spherical sources is here extended to ellipsoid sources, including the sphere and infinite cylinder as special cases. The cylindrical case is important because a swiftly moving, hot particle may act as a cylindrical igniting source. The theory assumes that the source instantaneously heats up a small volume and creates in it active particles (chain carriers). Under general assumptions as to the processes which occur (but without including the temperature dependence of reaction rates), the temperature distribution is obtained and from the behavior of the temperature at the center of the source, a condition for ignition is derived in the form of a relation between the physical quantities involved. The results are similar to those previously obtained, one of the important differences being that for the cylindrical source ignition can occur without chain branching and without thermal self-acceleration of the reaction.

IN a previous paper[1] the author gave a theoretical treatment of the ignition of gases by local sources in which the igniting source was assumed to be spherical. In the present work this treatment is extended to sources which are prolate (elongated) ellipsoids of revolution, including the sphere as a special case, and as another special case of particular interest, the infinite cylinder.

The motivation for this extension is as follows. There is some evidence for believing that when gases in coal mines are ignited by the explosive used to break down the coal, the igniting agent is often a hot particle shot out by the explosive, particularly in the case of blown out shots. If a fast moving, hot particle is actually the igniting source in a gaseous mixture, it might be expected to act not as a spherical source but rather as a cylindrical source. It would then appear to be of interest to carry through for the cylindrical source the analysis previously given for the spherical source. This problem was suggested to the author by S. L. Gerhard of the Bureau of Mines.

Now the region immediately affected by the passage of an electric spark is not generally spherical, but probably close to an ellipsoid in shape. Hence, the consideration of an ellipsoid igniting source is closer to physical reality for this case. Since the sphere and infinite cylinder are also included as limiting cases of the ellipsoid, this probably contains all the physically interesting geometric shapes for the problem of ignition of gases by local sources.

[1] H. G. Landau, Chem. Rev. **21**, 245 (1937).

PHYSICAL ASSUMPTIONS

The physical mechanism which is adopted for this treatment of ignition is the same as before[1] except for the shape of the igniting source. It is briefly restated here with the necessary changes.

In a combustible gaseous mixture there is a source capable of rapidly releasing energy within a small volume at a distance from the walls; for example, an electric spark or a fast moving hot particle. It is assumed that the energy instantaneously heats up an ellipsoid volume and also creates active particles, which are the chain carriers of the chain-reaction theory. The following processes then take place: There is a heat generating reaction which is assumed to proceed at a rate proportional to the concentration of active particles, but this concentration varies with distance and time because the active particles are diffusing through the gas, and in addition are increasing in number at a rate proportional to their concentration, i.e., chain branching is occurring.

The temperature of the ellipsoid tends to fall because of the conduction of heat away from it, and to rise because of the heat generated.

The criterion for ignition which is adopted here is that the temperature at the center of the ellipsoid shall not decrease.

It is also assumed that the diffusion coefficient of the active particles is equal to the thermometric conductivity (thermal conductivity divided by the specific heat per unit volume) of the gas through which they diffuse.

For some discussion of the significance and limitations of these assumptions, the reader is referred to the previous paper.[1] The most serious limitation is probably the assumption that the rates of the chain branching and heat generating reactions are independent of temperature.

The case of the infinite cylinder is obtained from that of the ellipsoid of revolution by allowing the ratio of the major axis to the equal axes to become infinite. The purpose of assuming the cylinder to be infinitely long is so that diffusion and heat conduction occur only perpendicular to the axis of the cylinder. Physically this means that the cylindrical source must be so long in comparison to its thickness that the effect of the ends is negligible at points not close to the ends.

Solution of Equations and Derivation of the Ignition Condition

We use cylindrical coordinates r, θ, z, with the surface of the ellipsoid being given by $r^2+(z^2/h^2)=R^2$ $(h \geqslant 1)$; for $h=1$ we have the sphere, and $h=\infty$, the cylinder.

The differential equation for the concentration of active particles is

$$\partial n/\partial t=\mu^2\nabla^2 n+\alpha n \tag{1}$$

with the initial condition

$$\left.\begin{aligned} &n=n_0 \text{ for } r^2+(z^2/h^2)<R^2 \\ &n=0 \quad \text{for } r^2+(z^2/h^2)>R^2 \end{aligned}\right\} \text{at } t=0, \tag{2}$$

where $n=n(r, z, t)$ is the concentration of active particles (n, as well as temperature, is independent of the angle θ because of axial symmetry),

t = time,

μ^2 = diffusion coefficient,

∇^2 = Laplacian operator, here $\nabla^2=\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)+\frac{\partial^2}{\partial z^2}$,

α = branching coefficient,

n_0 = initial concentration of active particles inside the ellipsoid (these are the active particles created by the source),

h = ratio of the major axis of the ellipsoid to the minor axis,

R = semi-minor axis of ellipsoid (radius of sphere or cylinder for $h=1$ or $h=\infty$).

Eq. (1) is the diffusion equation with the additional term αn giving the rate of increase of active particles.

The differential equation for the temperature is

$$\frac{\partial T}{\partial t}=\mu^2\nabla^2 T+\frac{Q}{c}n(r, z, t) \tag{3}$$

with the initial condition

$$\left.\begin{aligned} &T=T_1 \text{ inside the ellipsoid} \\ &T=T_0 \text{ outside the ellipsoid} \end{aligned}\right\} \text{at } t=0, \tag{4}$$

where

$T=T(r, z, t)$ is the temperature,

μ^2 = thermometric conductivity,

Q = quantity of heat generated in unit time by the action of each active particle,

c = specific heat per unit volume,

T_1 = initial temperature of the ellipsoid (due to the heat given off by the source),

T_0 = initial temperature of the gas outside the region affected by the source.

Eq. (3) is the usual heat conduction equation with the additional term Qn/c which gives the rate of heat generation, this being proportional to the concentration of active particles.

To solve these equations, consider the following equation:

$$\partial U/\partial t=\mu^2\nabla^2 U \tag{5}$$

with the initial condition

$$\left.\begin{aligned} &U=1 \text{ inside the ellipsoid} \\ &U=0 \text{ outside the ellipsoid} \end{aligned}\right\} \text{for } t=0. \tag{6}$$

It is possible to express n and T very simply in terms of the solution, $U(r, z, t)$, of this problem. By considerations similar to those used before,[1] we find that

$$n=n_0 e^{\alpha t}U(r, z, t), \tag{7}$$

$$T=T_0+\left(T_1-T_0+\frac{Qn_0}{c}\frac{e^{\alpha t}-1}{\alpha}\right)U(r, z, t). \tag{8}$$

It is easy to verify directly that these expressions for n and T satisfy (1), (2), and (3), (4), remembering that U satisfies (5) and (6).

The solution of the equation for U is known[2] and may be written as

$$U(r,z,t)=\frac{1}{(2\mu(\pi t)^{\frac{1}{2}})^3}\int_{-hR}^{hR}\int_0^{(R^2-\zeta^2/h^2)^{\frac{1}{2}}}\int_0^{2\pi}\times\exp\left[-\frac{r^2+\rho^2-2r\rho\cos\phi+(z-\zeta)^2}{4\mu^2 t}\right]\rho d\zeta d\rho d\phi, \quad (9)$$

the integration being over the interior of the ellipsoid. This integral may be expressed in various ways by the use of Bessel functions and certain definite integrals related to them. These expressions will not be written down because for the present purpose only the value of U at the origin is needed. We have

$$U(0,0,t)=\frac{1}{(2\mu(\pi t)^{\frac{1}{2}})^3}\int_{-hR}^{hR}\int_0^{(R^2-\zeta^2/h^2)^{\frac{1}{2}}}\int_0^{2\pi}\times e^{-(\rho^2+\zeta^2)/4\mu^2 t}\rho d\zeta d\rho d\phi. \quad (10)$$

This can be expressed in terms of the error function, defined by

$$\operatorname{erf} x=\frac{2}{\sqrt{\pi}}\int_0^x e^{-s^2}ds,$$

giving

$$U(0,0,t)=\operatorname{erf}\frac{hR}{2\mu\sqrt{t}}-\frac{e^{-R^2/4\mu^2 t}}{g}\operatorname{erf}\frac{ghR}{2\mu\sqrt{t}}, \quad (11)$$

where g is the eccentricity, $g=(h^2-1)^{\frac{1}{2}}/h$. We note that

$$\lim_{h\to 1}U(0,0,t)=\operatorname{erf}\frac{R}{2\mu\sqrt{t}}-\frac{1}{\mu(\pi t)^{\frac{1}{2}}}e^{-R^2/4\mu^2 t}$$

which is the result previously obtained for the sphere; and

$$\lim_{h\to\infty}U(0,0,t)=1-e^{-R^2/4\mu^2 t}$$

which is the value for the cylinder (this same value would, of course, be obtained by solving the equation for the cylinder).

To obtain the condition for ignition, consider the temperature at the origin; substituting from (11) in (8), we have

$$T(0,0,t)=T_0+\left(T_1-T_0+\frac{Qn_0}{c}\frac{e^{\alpha t}-1}{\alpha}\right)\times\left(\operatorname{erf}\frac{hR}{2\mu\sqrt{t}}-\frac{e^{-R^2/4\mu^2 t}}{g}\operatorname{erf}\frac{ghR}{2\mu\sqrt{t}}\right). \quad (12)$$

This changes with time at the rate,

$$\frac{\partial T(0,0,t)}{\partial t}=\left(T_1-T_0+\frac{Qn_0}{c}\frac{e^{\alpha t}-1}{\alpha}\right)\times\left(-\frac{R^2}{4\mu^2 t^2 g}e^{-R^2/4\mu^2 t}\operatorname{erf}\frac{ghR}{2\mu\sqrt{t}}\right)+\frac{Qn_0}{c}e^{\alpha t}\left(\operatorname{erf}\frac{hR}{2\mu\sqrt{t}}-\frac{e^{-R^2/4\mu^2 t}}{g}\operatorname{erf}\frac{ghR}{2\mu\sqrt{t}}\right). \quad (13)$$

To determine the relation which must hold between the physical constants in order to have $\partial T(0,0,t)/\partial t\gtrless 0$ put

$$x=R/2\mu\sqrt{t},$$

$$\alpha=m(2\mu/R)^2,$$

$$A=\frac{4(T_1-T_0)k}{Qn_0R^2}\quad (k=\text{thermal conductivity}=\mu^2 c).$$

Then,

$$\frac{\partial T(0,0,t)}{\partial t}=\frac{Qn_0}{cg}x^4e^{-x^2}\operatorname{erf} ghx\left[-A-\frac{e^{m/x^2}-1}{m}+\frac{e^{m/x^2+x^2}}{x^4\operatorname{erf} ghx}(g\operatorname{erf} hx-e^{-x^2}\operatorname{erf} ghx)\right]. \quad (14)$$

From this expression, it may be seen that we have $\partial T(0,0,t)/\partial t\gtrless 0$ if, and only if,

$$F(x)=\frac{e^{m/x^2+x^2}}{x^4\operatorname{erf} ghx}(g\operatorname{erf} hx-e^{-x^2}\operatorname{erf} ghx)-\frac{e^{m/x^2}-1}{m} \quad (15)$$

is not less than the constant A. Now $F(x)$ approaches $+\infty$ as x approaches 0 or ∞ (for $m>0$). By differentiation we find that $F(x)$ has a single minimum given by

$$m=x^2\left[x^2-2-\frac{ghxe^{-(ghx)^2}}{\sqrt{\pi}\operatorname{erf} ghx}+\frac{2x^2\operatorname{erf} ghx}{ge^{x^2}\operatorname{erf} hx-\operatorname{erf} ghx}\right]. \quad (16)$$

[2] See, for example, Frank and von Mises *Differentialgleichungen der Physik* (F. Vieweg, 1927), Vol. 2, p. 201.

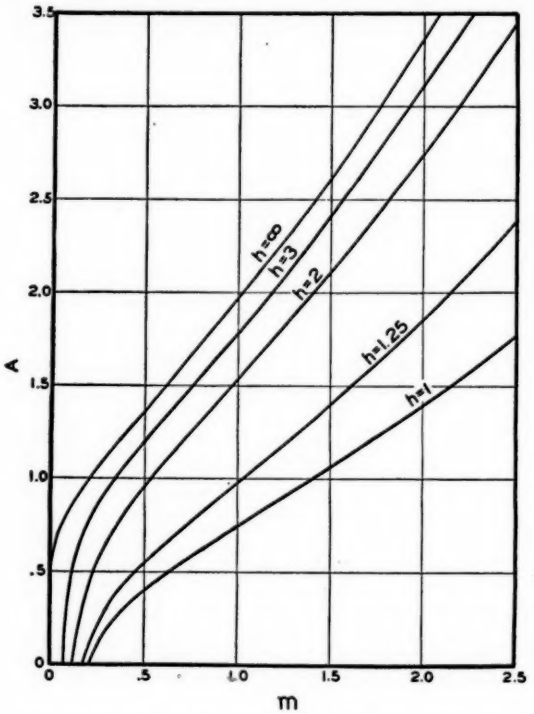

FIG. 1. Condition for ignition. Ignition occurs in the region between the curve and the line $A=0$.

$$A=4(T_1-T_0)k/Qn_0R^2;\quad m=\alpha(R/2\mu)^2;$$

h = the ratio of the major to the equal axes of the ellipsoid; $h=1$ for sphere, and $h=\infty$ for cylinder.

From this we can find the value of m which makes $F(x)$ a minimum for a given x, and the value of $F(x)$ at this minimum. From Eq. (14) it follows that $\partial T(0, 0, t)/\partial t \gtrless 0$ for all t, if and only if, A is not greater than this minimum value of $F(x)$.

We can, therefore, state the condition for ignition as follows: $A=4(T_1-T_0)k/Qn_0R^2$ must be less than or equal to a value depending on $m=\alpha(R/2\mu)^2$ and h (A is necessarily positive). The ignition limit is given by the equality in this relation.

Numerical values for the relation have been calculated for $h=1$, 1.25, 2, 3, and ∞ and are shown in Fig. 1.

DISCUSSION

It is immediately apparent from the figure that the results obtained here differ for the most part quantitatively, but not qualitatively, from those obtained for the sphere, so that most of the remarks in the previous paper[1] on the significance and applicability of this theory also apply here.

One of the important differences is in the behavior of the curve for the cylinder at $\alpha=0$, that is, when branching does not occur. It was found for the sphere, and this also holds for the ellipsoid, that ignition does not take place without branching. For the cylinder, on the contrary, ignition can occur without branching, the ignition condition being

$$A=4(T_1-T_0)k/Qn_0R^2 \leq \tfrac{1}{2}.$$

Thus, in this case, ignition occurs without any self-acceleration of the reaction. This would seem to be important because at sufficiently low temperatures both the branching rate and the thermal acceleration in combustible gas mixtures are small. This is a simpler relation than that which holds when there is a branching reaction, and it should be easier to test. A very long ellipsoid source behaves very much like a cylindrical source, and, as indicated in the figure, as the ellipsoid becomes more elongated the amount of branching necessary for ignition to be possible becomes smaller. It is to be remarked that if the temperature dependence of the reaction rates could be taken into account in the theory, it is quite possible that we would find that ignition may occur without branching in every case.

The increase in the size of ignition region with increase of h shown in the figure is due to the fact that this is a comparison of sources of equal strength per unit volume, but of increasing volume.

The qualitative part of the present result, that is, for ignition to occur

$$A=4(T_1-T_0)k/Qn_0R^2$$

must be less than a quantity depending on the branching rate, thermometric conductivity, and size and shape of the igniting source, is true for sources of even more general shape than those considered here (in the general case, R is a quantity proportional to a linear dimension of the source). However, the explicit evaluation of the relation given here for the sphere, ellipsoid, and infinite cylinder probably includes all that is of physical interest.

A Contribution to the Theory of Viscous Flow Reactions for Chain-Like Molecular Substances

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Ewell and Eyring investigated a relation for the coefficient of internal friction as a reciprocal reaction rate employing a large number of data. In this paper these investigations are extended to new data involving homologous series of higher esters. The variation of the activation heats of the flow process with temperature, molecular weight, and constitution, is considered and an attempt made to correlate it to the molecular constitution. There are indications that the above-mentioned ideas contain implicitly through Stefan's theorem a relation between surface tension and viscosity.

THE quantum mechanical transition-state method,[1] so successful for reaction kinetics, was applied by Eyring and Ewell[2] to the theory of transport phenomena in liquids. The flow process is considered as a chemical reaction, in which every molecule passes from one equilibrium position over a potential barrier in an adjacent one. The slower the reaction rate, the smaller the diffusion constant and the larger the viscosity.

In a large number of cases it could be shown that the activation energy of the "flow reaction" amounts to a more or less constant fraction $1/n$ of the internal evaporation energy. We shall later on revert to this point. Especially interesting are those cases like water, in which changes of n occur with the temperature. In this way, it is possible, under certain circumstances, to obtain information about changes of the internal state of the fluid, e.g. dissociation or association, respectively, and curling up of chain molecules.

These questions have a great scientific and technical importance for the recognition of the structure of pure liquids as well as of solutions. Last, but not least, is the investigation of fluids with long chain molecules, also important as a transition for the understanding of high molecular weight substances. These often cannot be kept in the melted nor in the dissolved state in consequence of the large molecular attraction.

It seemed desirable to examine the data of Albert and Eirich[3] on esters in the above-outlined direction. Moreover it is possible in this way, to furnish a semi-empirical relation between two quantities characteristic for the intermolecular forces, *viz.* the surface tension and the viscosity.

The reliability of the evaporation energies must be examined critically before employing them for the determination of the ratios evaporation energy/activation energy since they were determined semi-empirically rather than experimentally. The extrapolation of the Stefan factors in the $E_{\text{vap}}-\sigma$ relation in respect to molecular weights is burdened with an uncertainty even for the nonylic acid and naturally is greater for the esters of nonylenic and oleic acid. But the comparison of the results with the experimentally determined behavior of the paraffins and the consistency with the values for the evaporation heats resulting from the additivity rule, respectively, seem to eliminate the principal objections. That is also valid for the use of the factors for nonylic acid in the case of the esters of nonylenic acid. As the molecular surface tensions are equal, the boiling points and the evaporation energies of saturated and unsaturated compounds are similar, larger changes of the factors are not to be expected. The assumption of constant values for the several esters of the homologous series is in principle wrong, but

[1] A detailed report of this theory is found in Trans. Faraday Soc. **34** (1938). Compare also H. Mark and R. Simha, "Atomphys. Grundlagen d. chem. Katalyse," *Handbuch der chemische Katalyse* (J. Springer, Berlin, in press).

[2] H. Eyring, J. Chem. Phys. **4**, 283 (1936); R. H. Ewell and H. Eyring, *ibid.* **5**, 726 (1937), in the following designated with I, and II., R. H. Ewell, J. App. Phys. **9**, 252 (1938).

[3] O. Albert and F. Eirich, Zeits. f. physik. Chemie **A183**, 9 (1938).

the magnitude of the error is not significant. It will become evident at the end, that even greater uncertainties do not much influence the determination of the n values, and, avoiding all the uncertainties by employing molecular surface energies instead of evaporation heats, we do not change the nature of the conclusions.

In order to determine the activation energy E_{vis} of the flow process, we plot, as usual, $\ln k$, and in this case $\ln \eta$ against $1/T$. Fig. 1 shows these curves for the first three esters of the formic and acetic acid ($F_{1,2,3}$, $A_{1,2,3}$), for the propionic methylester and for allylacetate (P_1, $\bar{A}_3$), for the first three esters of nonylic and nonylenic acid ($N_{1,2,3}$, $\bar{\bar{N}}_{1,2,3}$), and finally for the first five esters of the oleic acid series (O_{1-5}). The data for the low molecular esters were taken from the Landolt-Börnstein tables, in order both to put our conclusions on a broader base and to have a transition from the substances treated in II to ours.

For the F, A and P esters and those of the nonylenic acid, one obtains with remarkable accuracy straight lines. For N_{1-3} and O_{1-5} the functions are represented by curves smoothly bent against the $1/T$ axis, which, however, have a practically constant slope in the region of about 300–400K. Similar curves were obtained by Eyring and Ewell for the paraffins higher than C_{10}. Unfortunately the given material provides too little data in order to draw the curves in an entirely definite way and to determine the differential quotients graphically. Therefore the difference quotient was first calculated in the approximately linear region. Then, for greater accuracy, representation of the temperature dependence of η by an analytical expression was tried, thus:

$$\eta = A T^s e^{Q/RT}. \tag{1}$$

Here A, s and Q are established as temperature independent parameters[4] and are computed from the three most distant points. Values of s of 3.5 to 5.5 mean a temperature dependence of the frequency number and therefore of the entropy of activation of the flow reaction. In calculating with the aid of the so-found values the fourth and further points of the curve, one finds discrepancies of no more than maximally 0.1 between measured (or graphically interpolated) and computed points.

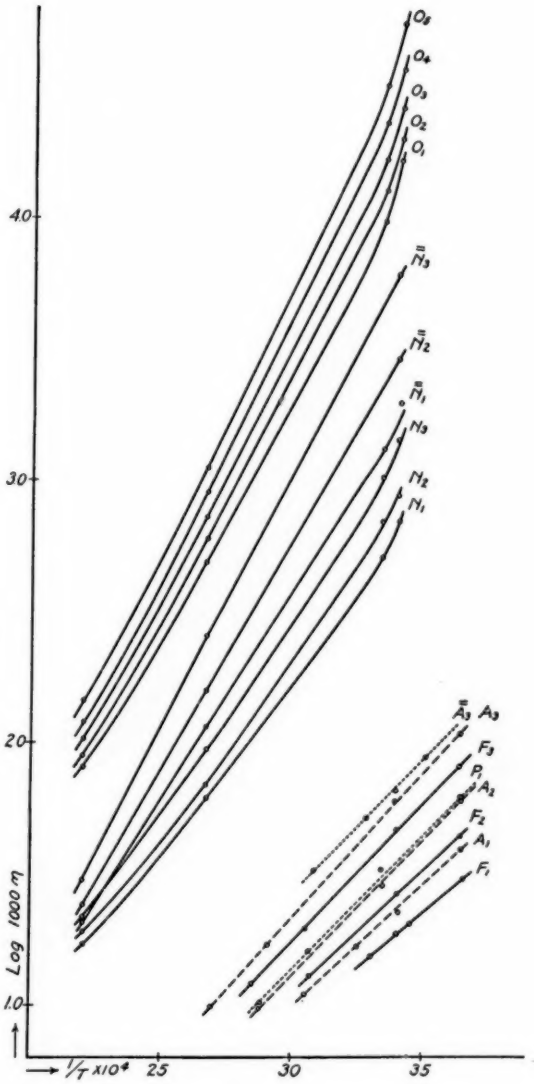

FIG. 1.

On principle it is further possible to apply the statistical methods for the calculation of the entropy factor, also to reactions of the kind considered in this paper, as did Eyring in I. However, several factors enter which are difficult to determine. Therefore here, as in II, an empirically given entropy of activation was assumed.

The activation heat of a monomolecular

[4] One has generally to assume a temperature dependence of Q and also of A; compare, for instance, E. N. da C. Andrade, Phil. Mag. **17**, 698 (1934) and A. G. Ward, Trans. Faraday Soc. **33**, 88 (1936). Considering the small curvature, this was not necessary.

transformation is defined by[5]

$$E=-R\frac{d\ln k}{d(1/T)}. \qquad (2)$$

For the flow reaction we obtain by consideration of (1)

$$E_{vis}=R\frac{d\ln\eta}{d(1/T)}=Q-sRT. \qquad (2a)$$

In the corresponding columns of the Tables I to IV the values of the calculated activation heats and directly determined activation heats, respectively, are found. Besides in the Tables II and IV the slopes of the straight regions are also indicated. The next column shows the ratios of evaporation and activation energies. As these ratios are mostly temperature dependent, the n values, given in the last column, were constructed at different corresponding temperatures, indicated in brackets; namely for a better comparison in the case of low boiling substances at the boiling point and $\frac{4}{5}$ of the boiling temperature, for higher boiling substances at $\frac{4}{5}$ and for further comparison with the still higher boiling oleic acid esters also at $\frac{3}{5}$ b.p. In determining the n we always rounded off to the next integer or half integer.

TABLE I.

Subst.	°K	E_{vap}	$E_{vis}=R\frac{\Delta\ln\eta}{\Delta\left(\frac{1}{T}\right)}$	$\frac{E_{vap}}{E_{vis}}$	n
Methyl Formiate	290	6.48	1.66_5	3.90	4 ($\frac{4}{5}$)
	303	6.26		3.76	3.5 (b.p.)
	313	6.06		3.64	—
Ethyl Formiate	273	7.37	1.87	3.94	4 ($\frac{4}{5}$)
	323	6.61		3.54	3.5 (b.p.)
Propyl Formiate	273	8.74	2.08_5	4.19	4 ($\frac{4}{5}$)
	353	6.97		3.34	3.5 (b.p.)
	363	6.75		3.24	—
Methyl Acetate	293	7.40	1.84	4.02	4 ($\frac{4}{5}$)
	333	6.54		3.55	3.5 (b.p.)
Ethyl Acetate	273	8.32	2.01	4.14	4 ($\frac{4}{5}$)
	353	6.86		3.42	3.5 (b.p.)
	373	6.53		3.25	—
Propyl Acetate	293	8.92	2.20	4.05	4 ($\frac{4}{5}$)
	373	7.41		3.37	3.5 (b.p.)
	383	7.22		3.28	—
Methylpropionate	313	7.68	1.98	3.88	4 ($\frac{4}{5}$)
	343	7.17		3.61	—
	353	6.97		3.52	3.5 (b.p.)

[5] R. C. Tolman, *Statistical Mechanics* (Chemical Catalogue Company, 1927), pp. 259–69; V. K. La Mer, J. Chem. Phys. **1**, 289 (1933).

TABLE II.

Nonylic acid ester	°K	$-T\cdot\frac{d}{dT}(\sigma v_m)^{\frac{1}{3}}$	$E^*_{vap}=F\cdot u_\sigma$	$R\frac{\Delta\ln\eta}{\Delta\left(\frac{1}{T}\right)}$	$E_{vis}=Q-sRT$	$\frac{E_{vap}}{E_{vis}}$	n
Methyl	298	789	13.2_2	2.70	3.1_0	4.2_6	4 ($\frac{3}{5}$)
	373	990	11.2_5		2.5_6	4.4_0	4.5 ($\frac{4}{5}$)
	453	1200	9.2_3		1.9_9	4.6_3	—
Ethyl	298	822	13.8_0	2.96	3.3_1	4.1_7	4 ($\frac{3}{5}$)
	373	1030	11.7_4		2.6_5	4.4_3	4.5 ($\frac{4}{5}$)
	453	1250	9.6_3		2.0_1	4.7_8	—
Propyl	298	860	14.4_8	3.10	3.3_9	4.2_7	4 ($\frac{3}{5}$)
	373	1077	12.3_0		2.9_0	4.2_4	4 ($\frac{4}{5}$)
	453	1309	10.1_0		2.3_8	4.2_4	—

* $u_\sigma=2.02\cdot[\sigma v_m^{\frac{1}{3}}-Td/dT(\sigma v_m^{\frac{1}{3}})]$; F (according to Albert and Eirich) for 298° = 3.72, 373° = 3.15, 453° = 2.60.

The data in the tables can be summarized as follows:

Table I. (a) The n vary from 3.5 at the b.p. to 4.0 at $\frac{4}{5}$ b.p. The ratios and therefore the n decrease with increasing temperature. Rounding off in the same way as Eyring did, one obtains in agreement with his results $n=4.0$. (b) The ratios at the b.p. decrease with increasing molecular weight.

Table II. (a) At $\frac{3}{5}$ b.p. results $n=4$, at $\frac{4}{5}$ b.p. $n=4.5$. At the boiling point we have therefore to expect $n=5$. (b) The ratios remain practically constant with increasing molecular weight. (c) With increasing temperature they increase a little.

Table III. (a) Surprisingly the ratios and n values at $\frac{3}{5}$ b.p. are 4, but decrease to 3.5 at $\frac{4}{5}$ b.p. and tend towards a limit 3. (b) They decrease also with increasing molecular weight.

Table IV. All the esters of oleic acid have $n=5$ at $\frac{3}{5}$ b.p. As the quotients remain almost constant against changes of the temperature, one cannot expect alterations of this value. Also with the molecular weight definite changes do not occur.

One has to try to relate the n values for the four groups to probable properties of the molecules or of the corresponding liquids. Ewell and Eyring find for molecules, which do not deviate much from the spherical form, a fraction $1/n=\frac{1}{3}$.

TABLE III.

NONYLENIC ACID ESTER	°K	$-T\cdot\frac{d}{dT}(\sigma v_m^{\frac{1}{3}})$	$E^*_{vap}=F\cdot u_\sigma$	$E_{vis}=R\frac{\Delta \ln \eta}{\Delta\left(\frac{1}{T}\right)}$	$\frac{E_{vap}}{E_{vis}}$	n
Methyl	298	762	13.2_2	3.09	4.2_8	4 ($\frac{3}{5}$)
	373	955	11.2_5		3.6_4	3.5 ($\frac{4}{5}$)
	453	1160	9.2_5		2.9_9	—
Ethyl	298	804	13.9_2	3.42	4.0_7	4 ($\frac{3}{5}$)
	373	1006	11.8_8		3.4_7	3.5 ($\frac{4}{5}$)
	453	1222	9.7_5		2.8_5	—
Propyl	298	823	14.5_0	3.73	3.8_9	4 ($\frac{3}{5}$)
	373	1030	12.3_0		3.3_0	3.5 ($\frac{4}{5}$)
	453	1251	10.0_5		2.6_9	—

* See Table II.

TABLE IV.

OLEIC ACID ESTER	°K	$-T\cdot\frac{d}{dT}(\sigma v_m^{\frac{1}{3}})$	$E^*_{vap}=F\cdot u_\sigma$	$R\frac{\Delta \ln \eta}{\Delta\left(\frac{1}{T}\right)}$	$E_{vis}=Q-sRT$	$\frac{E_{vap}}{E_{vis}}$	n
Methyl	298	966	20.6_0	3.67	4.4_5	4.6_2	5 ($\frac{3}{5}$)
	373	1208	17.6_5		3.6_4	4.8_5	
	453	1469	14.8_5		2.7_7	5.3_6	
Ethyl	298	987	21.1_5	3.88	4.4_1	4.8_0	5 ($\frac{3}{5}$)
	373	1234	18.0_5		3.7_4	4.8_2	
	453	1500	15.2_2		3.0_3	5.0_7	
Propyl	298	1010	21.8_0	3.96	4.4_3	4.9_2	5 ($\frac{3}{5}$)
	373	1263	18.5_3		3.8_1	4.8_7	
	453	1536	15.5_5		3.1_5	4.9_4	
Butyl	298	1058	22.5_5	4.12	4.6_3	4.8_2	5 ($\frac{3}{5}$)
	373	1322	19.2_7		3.9_7	4.8_5	
	453	1610	16.1_5		3.2_2	5.0_2	

* See Table II; F (according to Albert and Eirich) for 298° = 4.10, 373° = 3.50, 453° = 2.95.

Higher values originate from special bonds. Reductions are always found in the case of elongated molecules, possibly through preference of a flow direction. One has, therefore, to expect $n=3$ for symmetrical molecules, $n<3$ in the case of associations, while $n\sim4$ for elongated ones, perhaps through compensation of two influences: fixation by orientation against the greater facility for flow in the direction of the longest axis. Ewell and Eyring consider it remarkable that even from so elongated molecules as paraffins with 18C atoms only $n=4$ values result. They assume that above all the curled molecules are activated for the flow process.

Before applying these ideas to our results we have to mention a point overlooked by Ewell and Eyring, namely, the decreasing of n with rising temperature for normal substances as seen, for instance, from Table I. We believe this is caused by a certain quality of the model. The n decrease because the heats of evaporation show a temperature dependence in accord with Kirchhoff's theorem, while E_{vis} as activation heat remains, generally and for our material in many cases, constant over a large temperature range. These changes of n are likely to have no special importance for the flow process, but are only a consequence of the decrease of E_{vap}.

For N_{1-3} and $\overline{N}_{1-3}$ one obtains again $n=4$; for O_{1-5}, however, one obtains 4.5–5. In the first place it seems easy to explain this increase by assuming that the oleic acid esters are less curled up than the paraffins of the same chain length, which is plausible as consequence of the O−CO group and particularly of the double bond.

This explanation may be right in this or some other cases. Nevertheless it becomes more difficult the more data are considered.

It is, for instance, striking that the nonylenic acid esters behave differently from those of nonylic and oleic acid and show the same temperature dependence of E_{vis} and n as the low esters. Presumably this is connected with another remarkable fact, namely, that the double bond can raise quantities related to the cohesion forces as density or surface tension, while others as evaporation energies remain practically constant and the melting points decrease. Considering our present knowledge of the structure of long chain molecules, it is not impossible that the shape stretched by the double bond, allows for a closer packing in the fluid state in contradistinction to the behavior of low molecular compounds, where it lowers the density. Nevertheless, it is more difficult for these molecules to arrange in a lattice.

These considerations can be correlated to the fact, that the constant values of A and Q are presumably not real, but are rather a result of a contrary variation of the two quantities. The longer a molecule is, the more essential must be its shape, as described by the inner-molecular statistics for the entropy factor. Two mechanisms are conceivable. Following the first the distribution of more flattened and curled up molecules is changed in favor of the latter ones with rising temperature. Besides the equilibrium

between inter- and intramolecular forces will turn out in such a way that a deviation from the most probable shape in vacuum will occur. In order to utilize better the intermolecular fields, the molecules will take shapes which are statistically (referred to the vacuum) less probable, but potentially more favorably orientated.

The data in this paper are not as extensive as those of Eyring and Ewell, but on the other hand they comprise a larger temperature range and treat in more detail one special class of substances.

We obtain the following results:

(1) E_{vis} is $\frac{1}{3}$ to $\frac{1}{4}$ of E_{vap}, whereupon viscous flow can be understood as one dimensional evaporation process, sometimes facilitated through orientation.

(2) ln η as logarithm of a reciprocal reaction rate varies linearly with $1/T$. E_{vis}, therefore, is constant and is not a temperature independent fraction of E_{vap}.

(3) Under the influence of the temperature dependence of the shape of long chain molecules, E_{vis} as well as the entropy factor can be temperature dependent or finally the compensating action of both can be disturbed. The graph ln η *vs.* $1/T$ is no more a straight line and n can change with T in any way.

One gets the following explanation for the behavior of our substances. For the shorter esters as normal liquids the points (1) and (2) are valid. For the longer nonylic acid esters and the paraffins, one must also consider point (3). It is plausible that the n values in this case increase with the temperature and that therefore E_{vis} decreases more quickly than E_{vap}, in respect to the small association always present in such long molecular substances. In this way, the contradiction that the n values of the curled-up molecules increase with temperature instead of decreasing, which was not observed by Eyring, since his considerations were restricted to a small temperature range, no longer exists. It may be noticed that the value $n=4$ discussed in II for paraffins applies only for the chosen temperature which in no way corresponds to the temperature at which the other factors were determined.

Following these ideas, one can easily understand the behavior of the unsaturated esters. In the case of the nonylenic acid esters the double bond divides the molecules in two parts which are so short that the bending is not an important factor. Therefore these substances behave in respect to the absolute values as well as the changes in temperature of the n very similarly to the shorter esters. The slight differences are presumably connected with the fact that the first substances are saturated and that the determination of corresponding states for saturated and unsaturated fluid substances is doubtful in taking into account the irregular melting points.

The similarity in the behavior of the oleic acid and the nonylic acid esters is attributable to the fact that the parts of the former which are formed by the double bond are approximately just as long as the entire molecules of the latter and therefore possess sufficient internal mobility. The large, almost linear range between approximately 300–400K, which is caused by a similar, but less complete compensation than that of the normal substances, is delimited by two curvatures. One has to assume two different effects, namely, at room temperature the existence of a small association[6] and at higher temperatures the effects of temperature upon the shape.

The activation energies show a rather regular increase with the molecular weight. The ratios E_{vap}/E_{vis}, on the contrary, decrease for $\overline{\overline{N}}_{1-3}$ and the lower esters, and remain almost constant for the other substances. In the latter case the evaporation heats increase in the same way as the activation heats, but in the former case for the shorter and more rigid molecules, they increase more slowly. These as well as the former considerations show that although a far-going analogy between evaporation and flow reaction may exist, characteristic differences in details occur. We mention this self-evident fact in the hope that if we pursue these differences, they will furnish further information about the mechanisms occurring in fluids.

Finally, formula (1) gives a relation between the surface tension of a fluid and its viscosity. For the internal evaporation heat is connected with the surface energy by means of the relation

$$E_{vap}=F[\sigma v_m^{\frac{2}{3}}-T(d/dT)(\sigma v_m^{\frac{2}{3}})],$$

[6] E. E. Walker, Phil. Mag. **47**, 513 (1924).

where the Stefan-factor F is temperature dependent and has to be determined empirically in every special case. Nevertheless, it does not vary much for the most normal substances and for temperatures between 20 and 150°C, namely, from about 2.5 to 3.5. Therefore, F can be cancelled approximately against n in the expression $E_{vis}=E_{vap}/n$ or replaced by values between 0.7 and 1. (For our esters 0.84–0.93 for room temperature.) It means that the activation energy in the straight part of the curves is nearly equal to the molecular surface energy and therefore;

$$\eta=A \exp\{[\sigma v_m^{\frac{1}{3}}-T(d/dT)(\sigma v_m^{\frac{1}{3}})]1/RT\}. \quad (3)$$

By this fact our conclusions are also freed from the assumptions made in determining the evaporation energies and could in a similar way be discussed in terms of surface energies in the place of evaporation heats.

We wish to thank Professor Victor K. La Mer for many helpful discussions.

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Intensities of Electronic Transitions in Molecular Spectra

III. Organic Molecules with Double Bonds. Conjugated Dienes

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This paper is the first of a series on the application of intensity calculations to the spectra and related properties of organic compounds containing conjugated or resonating double bonds. It is concluded that in most cases the characteristic strong absorption of such compounds (giving color if the number of conjugated double bonds is large enough) is due to an $N\rightarrow V$ transition (homopolar normal state→ionic excited state) similar to those already identified in paper II for I_2, O_2, C_2H_4, and other molecules.

The present paper is devoted primarily to conjugated dienes. Unconjugated dienes and polyenes are treated incidentally, and it is shown theoretically that their ultraviolet spectra should be similar to those of alkenes (C_2H_4 and derivatives). There should be no strong absorption peak above λ2000, and the intensity per double bond should be about the same as in alkenes. These conclusions are in agreement with the rather scanty experimental data (examples, diallyl, rubber).

Detailed calculations are made on 1, 3-butadiene by the molecular orbital method, assuming all the atoms to be in one plane. The results are applicable also to other conjugated dienes. Four $N\rightarrow V$ transitions must occur for the *unsaturation* electrons, i.e., those electrons which make the second or weaker bond in double bonds. This group of four transitions corresponds to the one $N\rightarrow V$ transition in alkenes; according to the calculations, the total absorption intensity per double bond is considerably increased by conjugation, especially if the molecules are in the trans-form. Conjugation causes the frequencies of the four transitions to scatter toward both longer and shorter wave-lengths as compared with alkenes, as Hückel's work implicitly shows. Although the calculated frequencies of the four transitions are independent of the shape of the molecule (within the range of reasonable assumptions), their intensities are very different for the cis- and trans-forms, and are also very sensitive to the bond angles. There is a marked tendency for the intensity to concentrate in the longer wave-length at the expense of the shorter wave-length $N\rightarrow V$ transitions, especially for the trans-form. In the latter, nearly all the intensity is concentrated in the longest wave-length of the four $N\rightarrow V$ transitions. This gives an essential clue to the explanation of the spectra of molecules containing conjugated polyene chains, e.g., carotene and related pigments, as will be shown in VI of this series.

Comparison of the theoretical predictions with available data on the ultraviolet spectra of dienes shows in general good agreement if we suppose that butadiene and its derivatives exist in the trans-form, except that perhaps its centrally-substituted derivatives (e.g., isoprene) exist partly in the cis-form. This conclusion is in line with other evidence. The available data are, however, somewhat conflicting, and systematic new measurements on the ultraviolet spectra of dienes and polyenes would be extremely valuable. The cyclic dienes, which are necessarily *cis*, show much weaker absorption in their longest wave-length $N\rightarrow V$ absorption region than do the open-chain dienes, just as predicted; the cyclopentadiene absorption is half as strong as that of cyclohexadiene, also as predicted in view of the different bond angles in the two rings. The absorption in both these molecules, begins, however, at abnormally long wave-lengths. This can be explained by

"hyperconjugation," as will be shown in IV of this series.

Application of the electron-pair bond method to the problem of the spectra of polyenes is briefly discussed. Sklar has suggested that transitions to excited states which are predicted by consideration of resonance among *neutral* canonical structures can account for long wave-length absorption and color in organic compounds. It is here tentatively concluded, however, that such transitions are probably in general weak, and that they are not always the longest wave-length absorption transitions.

1. Introduction

In two previous papers[1, 2] the writer has discussed the theoretical calculation of absolute intensities in molecular spectra, and has shown that significant results can be obtained even with the available roughly approximate wave functions. As examples of molecules containing double bonds, oxygen, ethylene and some of its derivatives, and benzene were treated in the second paper.

The object of the present and following papers III–VII is to extend the calculations to examples of several types of organic molecules containing double bonds. This is of considerable interest, since it appears to be generally recognized that a large part of the visible and ordinary ultraviolet spectra of organic compounds are associated with the presence of double bonds, especially conjugated or resonating systems of double bonds.

In particular, Sklar has explicitly attributed color in organic compounds to transitions between levels which arise from resonance among different double-bonded structures, and has made some calculations supporting this view.[3] However, Sklar noted that in benzene, transitions from the ground state to some of the lower excited levels resulting from resonance are forbidden by electronic selection rules, and are actually represented only by very weak bands. Also for other molecules containing double bonds, it will be shown below that transitions to excited levels derived from resonance among neutral structures probably are not ordinarily responsible for strong transitions and intense color. On the other hand, Pauling, proceeding from a paper by Bury,[10] has recently given a quantum-mechanical explanation to long standing ideas of organic chemists in regard to the cause of intense color in certain types of dyes in which there is resonance between two structures differing in the location of an electron or positive charge in the molecule.[4] Pauling's brief discussion constitutes the first recognition on a quantum-mechanical foundation of the class of spectra designated as charge-resonance spectra by the writer in II.[2]

The main result of the present work is that for intense transitions in the visible or nearer ultraviolet it is generally necessary that the excited states shall have ionic (though not necessarily polar), wave functions, in such a way that the absorption process involves either transfer or resonance of electrical charge between one atom and another in the molecule.

To be sure, intense transitions *can* occur without charge transfer (particularly, transitions of Rydberg series type[2]); but it so happens that in organic molecules, most such transitions may be expected only in the vacuum ultraviolet region, or at least not in the visible.

It may also be well to mention that transitions do occur in the ordinary ultraviolet in organic molecules which are neither Rydberg series transitions nor of the types considered in the present paper. For example, the weak but characteristic aldehyde and ketone bands near λ2800 are probably analogous to certain perpen-

[1] R. S. Mulliken, J. Chem. Phys. **7**, 14 (1939). Hereafter referred to as I.

[2] R. S. Mulliken, J. Chem. Phys. **7**, 20 (1939). Hereafter referred to as II. The calculated f values which in II were called "theoretical" are for the most part really not purely theoretical, since they were based on theoretically calculated Q's combined with *empirical* ν's. This applies both to the AO and to the LCAO MO calculations. Really theoretical f values would use theoretically calculated ν's. This should be kept in mind when one is interested in a critical comparison of the merits of the AO and LCAO approximations from a theoretical standpoint. Hereafter, f values based on theoretical Q's and empirical ν's will be called "semi-theoretical."

In II it was concluded that the LCAO semi-theoretical f values are, in general, too large. From this it was deduced, under the tacit assumption that the semi-theoretical f values are real theoretical f values, that the LCAO Q^2 values are in general too large. Although this conclusion must still be accepted, it is of interest to note that if theoretical ν values had also been used, it might have turned out that the error in the theoretical Q^2 values is in part compensatory to error in the ν values, so far as f values are concerned.

[3] A. L. Sklar, J. Chem. Phys. **5**, 669 (1937). Also T. Förster, Zeits. f. physik. Chemie **B41**, 287 (1938).

[4] L. Pauling, in H. Gilman, *Organic Chemistry* (John Wiley & Sons, 1938) Vol. II, pp. 1888–9.

dicular-type transitions which are important in the spectra of halogen and halide molecules (see later paper); or possibly they are of a type forbidden by the electronic selection rules.[5]

The orbitals occupied by double-bond electrons are of two kinds, the first kind being essentially the same as occurs in single bonds, the second being characteristic of double bonds. The outstanding feature of these special double-bond orbitals is that they enforce a plane arrangement of all atoms directly connected to the double bond, or involved in a system of conjugated or resonating double bonds.

These orbitals appear in somewhat different guise according to whether we use the AO (atomic orbital) or the MO (molecular orbital) approximation for the wave functions. In the AO approximation, each atom participating in a double bond furnishes ordinarily one electron in an AO which Hückel[6] called $[p_h]$, Hund and others have called π, still others have called p_z, and the writer has called p_z or x.[7] The AO in question is a $2p$ orbital with its nodal plane in the plane of atomic centers which is determined by the double bond or bonds.

In the MO approximation, the characteristic double-bond electrons occupy one or more MO's every one of which has a nodal plane in the plane determined by the double bonds. If there is just one double bond as in C_2H_4, the two characteristic double-bond electrons occupy in the ground state "N" of the molecule one characteristic bonding MO. There is then also a second, antibonding, characteristic double-bond MO to which one of the electrons can be excited by absorption of light of suitable wave-lengths near λ2000, giving an excited singlet state "V". Such an electronic transition is then of the "$N \rightarrow V$" kind with which we shall here mainly deal. The $N \rightarrow V$ transition of C_2H_4 has already been discussed in II.[2] It was there shown that *in AO approximation* state V is of ionic character, while N is predominantly non-ionic.

In more complex systems of resonating or conjugated double bonds, there are several different occupied double-bond MO's, together with other normally unoccupied double-bond MO's to which double-bond electrons can be excited.[6] As a result there are several V states and several $N \rightarrow V$ transitions. It is such spectra in which we are here mainly interested.

A useful name introduced by Lennard-Jones[8] for electrons occupying the characteristic double-bond MO's is "mobile electrons." This is rather appropriate because these electrons, according to the MO approximation, can move throughout the plane system of atoms connected by the conjugated or resonating double bonds. [Further implications should not, however, be read into the word "mobile." Strictly speaking, the "mobile" electrons are merely *more* mobile than the others.] [*Added in proof.*] For the later papers of this series (see IV), the writer has decided to abandon the expression "mobile" electrons in favor of "unsaturation" electrons. The latter expression seems to be open to fewer objections than the former, and has the advantages that its meaning is rather self-evident, and that its use can properly be extended to triple bonds.

The reason why the mobile double-bond electrons give longer wave-length spectra than other electrons is essentially as follows:[8a] These mobile electrons are on the whole considerably less strongly bonding than other bonding electrons in organic molecules. Now it is a well-known rule[9] that, other things being equal, electrons which are less strongly bonding in the chemical sense are *less tightly bound* in the spectroscopic sense,—that is, they are more easily ionized. [More properly, the last two sentences might be replaced by corresponding statements about the bonding mobile-electron MO's which are occupied by electrons in the normal state of the molecule, rather than about the electrons themselves.] At the same time, the unoccupied antibonding MO's which correspond to the occupied bonding MO's of the mobile electrons are less strongly antibonding than antibonding MO's which correspond to other bonding MO's, and so are *more tightly bound* spectroscopically.[9] When,

[5] Cf. R. S. Mulliken, J. Chem. Phys. **3**, 564 (1935).

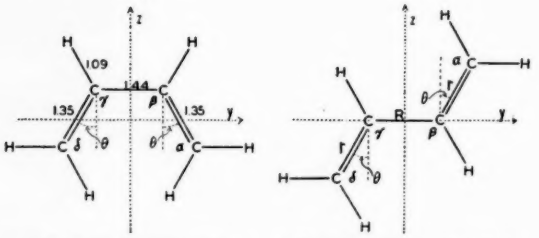
[6] E. Hückel, Zeits. f. Physik, **60**, 423 (1930); **70**, 204 (1931); **76**, 628 (1932); **83**, 632 (1933); and elsewhere. For an excellent review, E. Hückel, Zeits. f. Elektrochemie **43**, 752, 827 (1937).

[7] R. S. Mulliken, Phys. Rev. **41**, 75 (1932); **43**, 297 (1933); J. Chem. Phys. **3**, 522 (1935).

[8] J. E. Lennard-Jones, Proc. Roy. Soc. **158A**, 280 (1937).

[8a] E. Hückel in his 1937 review, reference 6, has already discussed this matter.

[9] R. S. Mulliken, Phys. Rev. **46**, 551 (1934); J. Chem. Phys. **3**, 514 (1934); also J. Chem. Phys. **3**, 522 (1935) on C_2H_4.



a. Cis-form (symmetry C_{2v}) *b*. Trans-form (symmetry C_{2h})

FIG. 1. Conceivable forms of 1,3-butadiene. Numerical values (reference 14) of the long and short C−C bond distances R and r (Fig. 1*b*) are given in angstroms in Fig. 1*a*. The angle θ of Eqs. (6) *et seq* is shown; in Fig. 1 as drawn here, θ is about 30°.

therefore, we consider transitions from occupied bonding MO's to unoccupied antibonding MO's, the energy difference is a minimum if the transition is performed by one of the *mobile electrons*, and so the corresponding spectrum comes at relatively long wave-lengths.

However, even the spectrum of the mobile electrons occurs at wave-lengths near and below λ2000 for molecules with isolated carbon-carbon double bonds.[2, 7] Conjugation and resonance are of decisive importance in pushing absorption to longer wave-lengths and so making double bonds effective as chromophoric groups; auxochromes act to promote resonance in certain ways.[10] The ways in which conjugation and resonance act to increase absorption wave-lengths are in part implicit in the papers of Hückel, especially in his work using the MO method;[6] in part Sklar has discussed some of them.[3] The present papers are intended to clarify them further, particularly as regards the explanation of the occurrence of *intense* absorption at long wave-lengths.

In III and following papers, examples of several types of molecules illustrating conjugation and resonance will be considered. Some of the examples are of additional interest in that their discussion leads to interesting predictions on relations between spectra and constitution. The discussion also leads to apparently valuable contributions toward explaining the refractivities of molecules with double bonds (Paper VI).

2. Butadiene (Molecular Orbital Method)

As one of the simplest examples of systems containing conjugated double bonds, we may take 1,3-butadiene ($CH_2=CH-CH=CH_2$). The results obtained can be applied without much modification, as we shall see, to other conjugated dienes, and extended without difficulty to conjugated polyenes. The quantum-mechanical structure of 1,3-butadiene and related molecules has already been discussed by several authors.[11]

It may safely be assumed that all the atoms lie in a plane, and it is probable, from both empirical and theoretical indications, based on experience with other organic molecules, that all bond angles (both H−C−H and −C−C−H) are near 120°. It is, however, not immediately clear to which of the two following configurations ("*cis*" and "*trans*," Fig. 1) the stable form of the molecule should belong. As we shall see below, the observed ultraviolet spectrum,[12] in agreement with other information, indicates that 1,3-butadiene itself exists normally in the trans-form, but that some of its derivatives have the cis-form.

In the following discussion we shall use first and mainly the LCAO MO approximation,[2] but at the end we shall make brief comparison with results obtained using AO's. Throughout the discussion of butadiene, we shall consider explicitly only the four mobile electrons connected with the two double bonds, since for our purposes the other electrons merely help to determine the Hartree force field in which the mobile electrons move.[6, 8]

It is best to carry on a parallel development of the theory for the cis- and trans-forms of the molecule. We may choose axes y and z as shown in Fig. 1, with the x axis perpendicular to the plane of the paper. We observe that the cis-form has symmetry C_{2v}, the trans-form C_{2h}. For convenience of reference, the conventional symbols for the various different possible species of MO's and of electronic states, for each of these two symmetries, are reviewed in Table I.

Let the four carbon atoms be lettered as in Fig. 1, and let ϕ_α, ϕ_β, ϕ_γ, ϕ_δ, stand for $2p_x$ carbon atom AO's on atoms α, β, γ, and δ, respectively. From these we can construct four LCAO MO's

[10] C. R. Bury, J. Am. Chem. Soc. **57**, 2115 (1935); also reference 4.

[11] E. Hückel, especially Zeits. f. Physik **76**, 630, 635–6, 640–1 (1932), and Zeits. f. Elektrochemie **43**, 775–7 (1937); L. Pauling and J. Sherman, J. Chem. Phys. **1**, 682 (1933); J. E. Lennard-Jones, Proc. Roy. Soc. **158A**, 293–5 (1937); W. G. Penney, Proc. Roy. Soc. **158A**, 318 (1937).

[12] G. Scheibe and H. Grieneisen, Zeits. f. physik. Chemie **25B**, 54 (1934).

TABLE I. *Orbital and state species characterizations.*

SYMMETRY C_{2v}					SYMMETRY C_{2h}				
SPECIES SYMBOL	SYMMETRY OPERATIONS E	$C_2(z)$	σ_y	σ_x	SPECIES SYMBOL	SYMMETRY OPERATIONS E	$C_2(x)$	i	σ_x
$A_1; z$	1	1	1	1	A_g	1	1	1	1
A_2	1	1	−1	−1	$A_u; x$	1	1	−1	−1
$B_1; x$	1	−1	1	−1	B_g	1	−1	1	−1
$B_2; y$	1	−1	−1	1	B_u	1	−1	−1	1

Explanation: C_2 refers to a 180° rotation around the axis indicated, σ to a reflection in the plane indicated, i to inversion at the center. The numbers +1 or −1 indicate how the various species of wave functions behave under the various symmetry operations. The capital letter symbols refer to complete several-electron wave functions or states; corresponding small letter symbols (a_1, a_2, etc.) are used for MO's. The letters x, y, z refer to the behavior of the coordinates or of the corresponding electric moment components; for example, the coordinate x and the corresponding electric moment component, for symmetry C_{2v}, behave like B_1. For further explanation, cf. R. S. Mulliken, Phys. Rev. **43**, 288 (1933).

χ_1, χ_2, χ_3, and χ_4 for the mobile electrons, all of the following general form:

$$\chi_i = \alpha_i\phi_\alpha + \beta_i\phi_\beta + \gamma_i\phi_\gamma + \delta_i\phi_\delta. \qquad (1)$$

Let the χ's be numbered in order of increasing energy. It is seen from considerations of symmetry that in general $\alpha_i = \pm\delta_i$ and $\beta_i = \pm\gamma_i$. In particular for χ_1 all the coefficients are positive, with $\alpha_1 = \delta_1$ and $\beta_1 = \gamma_1$, and there is bonding between all pairs of atoms. For χ_2, α_2 and β_2 are positive, γ_2 and δ_2 are negative; this gives bonding between atoms α and β and between γ and δ, but antibonding between β and γ. In the normal state of butadiene, two mobile electrons occupy χ_1 and two occupy χ_2. Eq. (1) and all the relations just stated are valid equally for the cis- and for the trans-form of butadiene.

The orbitals χ_3 and χ_4 are occupied only in excited states; χ_3 has $\alpha_3 = \delta_3$ positive, $\beta_3 = \gamma_3$ negative, giving bonding between atoms β and γ, but antibonding between α and β and between γ and δ. Finally, χ_4 has α_4, β_4, γ_4, δ_4 alternately positive and negative in sign, giving antibonding between the members of every pair of adjacent atoms. The spectra in which we shall be interested correspond to the transition of an electron from one of the occupied χ's (either χ_1 or χ_2) to one of the unoccupied χ's (either χ_3 or χ_4). The longest wave-length transition should be for $\chi_2 \rightarrow \chi_3$.

The MO's χ_1, χ_2, χ_3, χ_4, belong, respectively, to the orbital species b_1, a_2, b_1, and a_2 in the case of cisbutadiene, to the species a_u, b_g, a_u and b_g for transbutadiene (cf. Table II). The several coefficients α_i and so on for each χ_i in Eq. (1) are partly determined by symmetry, with the results stated above. Their exact values depend, however, on the detailed form of the force field for the mobile electrons. Since this cannot easily be determined, it is necessary to resort to approximations.

TABLE II. *Forms and energies of LCAO MO's of 1,3-butadiene.*

NAME OF MO[1]		COEFFICIENTS IN EQ. (1)[1, 2]				
CIS-FORM	TRANS-FORM	α_i	β_i	γ_i	δ_i	RELATIVE ENERGY[3]
$\chi_1 b_1$	$\chi_1 a_u$	v	w	w	v	$-\lambda\epsilon$
$\chi_2 a_2$	$\chi_2 b_g$	w	v	$-v$	$-w$	$-\mu\epsilon$
$\chi_3 b_1$	$\chi_3 a_u$	w	$-v$	$-v$	w	$\mu\epsilon$
$\chi_4 a_2$	$\chi_4 b_g$	v	$-w$	w	$-v$	$\lambda\epsilon$

[1] While the names and certain spectroscopic properties of the MO's differ for the cis-form (symmetry C_{2v}) and the trans-form (symmetry C_{2h}), the coefficients in Eq. (1) are the same for any given numbered χ regardless of the symmetry.

[2] The numerical values of the coefficients, it is found, can all be expressed in terms of two constants v and w. In the approximation of *no conjugation* ("Case I"), $v = w$; if we neglect overlapping integrals in normalizing the coefficients (this makes only a relatively small difference in the Q values to be calculated below), we have $v = w = \frac{1}{2}$. With a similar neglect we have [15] for the Lennard-Jones approximation ("Case II"), $v = 0.401$, $w = 0.582$. [In Hückel's approximation[13] with similar neglect of overlapping integrals, $v = 0.372$, $w = 0.601$.]

[3] The energies of all the orbitals are given (for any one of the approximations) by an additive constant (cf., e.g., Hückel[13]), plus the multiple of ϵ indicated in the table; $-\epsilon$ is the value of the resonance integral, identical with Hückel's "β," *evaluated for the normal double-bond distance* $r = 1.34$A. For Case I, $\lambda = \mu = 1$; in Case II, $\lambda = 1.422$, $\mu = 0.674$.[16] [In the Hückel approximation,[13] $\lambda = 1.618$, $\mu = 0.618$.]

If the four carbon atoms in Fig. 1 are assumed to have equivalent force fields for the mobile electrons, and the distances r and R of Fig. 1 are assumed equal, the coefficients and energies of the four MO's are readily obtained. This has been done by Hückel (see Table II).[13] A probably better approximation has been worked out by Lennard-Jones, who finds $r = 1.35$A, $R = 1.44$A by theoretical MO calculations.[14] Penney gets the same values of r and R by AO calculations.[14] While Lennard-Jones[8] gives only the *energies* of

[13] E. Hückel, Eq. (6) and Table on p. 636, in reference 11. More explicitly: the coefficients and energies given in detail by Hückel in Zeits. f. Physik **70**, 268 (1931) for 1,2-dihydrobenzene are equally applicable, in the approximation used, to 1,3-butadiene or any other conjugated diene. E. Hückel, Zeits. f. Elektrochemie **43**, 775–7 (1937).

[14] The values $r = 1.35$A, $R = 1.44$A are each 0.01A greater than those calculated by Lennard-Jones[11] and by Penney.[11] This change is based on the fact that the most reliable present value of the C=C distance in C_2H_4 is 1.34A (cf. L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **59**, 1223 (1937)), whereas Lennard-Jones and Penney assumed 1.33A.

the four MO's, the corresponding coefficients are easily obtained (see Table II).[15, 16]

Although Lennard-Jones' calculation still involves simplifying assumptions and a somewhat uncertain empirical parameter ϵ_R/ϵ_r, we may take it as giving an acceptable approximation to the LCAO approximation. Let us call this "Case II." As a second hypothetical case, much farther from the truth but interesting for comparison, let us assume that the two double bonds of Fig. 1 are not conjugated, that is, that they interact only to a very slight extent. Then r and R would have the normal distances 1.34A and 1.54A characteristic of ordinary double and single bonds, respectively. In this "Case I" it is seen that the four coefficients in Eq. (1) are all equal in numerical value, for each of the χ's. In both cases, the following intensity calculations are applicable equally to the cis- and to the trans-form of butadiene, and also to other conjugated dienes.

We now consider the various excited states obtainable by excitation of a single one of the mobile electrons to an unoccupied mobile-electron MO. These and the normal state N may be described as follows:

$$\left.\begin{array}{ll} N\text{: } (\chi_1)^2(\chi_2)^2, & {}^1A_1 \text{ or } {}^1A_g \\ T_1,\ V_1\text{: } (\chi_1)^2(\chi_2)(\chi_3), & {}^{3,1}B_2 \text{ or } {}^{3,1}B_u \\ T_2,\ V_2\text{: } (\chi_1)^2(\chi_2)(\chi_4), & {}^{3,1}A_1 \text{ or } {}^{3,1}A_g \\ T_3,\ V_3\text{: } (\chi_1)(\chi_2)^2(\chi_3), & {}^{3,1}A_1 \text{ or } {}^{3,1}A_g \\ T_4,\ V_4\text{: } (\chi_1)(\chi_2)^2(\chi_4), & {}^{3,1}B_2 \text{ or } {}^{3,1}B_u. \end{array}\right\} \quad (2)$$

The state symbols ${}^1A_1$, ${}^3B_2$, and so on are obtained from the MO species symbols in the usual way (cf. reference at end of Table I); for the MO species symbols of the various χ's, see Table II. In Eq. (2), the state symbols given first are valid if the molecule is *cis*, those given second if it is *trans*. Transitions from state N will occur with considerable intensity of course only to the *singlet* states V_1 ${}^1B_2$ or ${}^1B_u$ and so on, and only very weakly to the triplet states T_1 ${}^3B_2$ or ${}^3B_u$ and so on. Presumably each T state has lower energy than the corresponding V state.

Considering now the electronic selection rules (cf. reference at end of Table I), a striking difference appears between the *cis* and *trans* isomers. For the former, the transitions $N\rightarrow V_1$, $N\rightarrow V_2$, $N\rightarrow V_3$, $N\rightarrow V_4$ are all allowed, the first and last with electric moment vibrating in the y direction (cf. Fig. 1), the other two with z electric moment. But for the *trans* isomer, only $N\rightarrow V_1$ and $N\rightarrow V_4$ are allowed. This is in spite of the fact that the *frequencies* of the several transitions should differ very little for the two isomers.

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[15] The values of v and w for the Lennard-Jones approximation were obtained as follows. First setting up the expression

$$E_i = \int \chi_i H \chi_i dv$$

for each of the χ's, with coefficients expressed in terms of v and w as in Table II, we obtain, after neglecting the same small terms as are neglected by Lennard-Jones,[8]

$$(E_{1,4} - E_0) = \alpha_d + 2w_i^2\alpha_s \pm 2w_i^2\beta_s \pm 4v_iw_i\beta_d,$$
$$(E_{2,3} - E_0) = \alpha_d + 2v_i^2\alpha_s \mp 2v_i^2\beta_s \pm 4v_iw_i\beta_d,$$

where α and β stand for a Coulomb and a resonance integral, respectively, and the subscripts s and d, respectively, refer to the long and the short C−C distance (1.44A and 1.35A[14]). [The upper signs refer to E_1 or E_2, the lower to E_4 or E_3.] If with Hückel and Lennard-Jones we neglect the end-atom effect on the α's by putting

$$\alpha_d + 2w_i^2\alpha_s = \alpha = \alpha_d + 2v_i^2\alpha_s,$$

we obtain the following expressions for the quantities $E_i - E_0 - \alpha$:

$$E_{1,4} - E_0 - \alpha = \pm 2w_i^2\beta_s \pm 4v_iw_i\beta_d$$
$$E_{2,3} - E_0 - \alpha = \mp 2v_i^2\beta_s \pm 4v_iw_i\beta_d.$$

Since these expressions correspond to the same simplifying assumptions as Lennard-Jones made, they may be set equal to the solutions $\pm\frac{1}{2}[\beta_s \mp (\beta_s^2 + 4\beta_d^2)^{\frac{1}{2}}]$ given by him. For example,

$$2w_i^2\beta_s + 4v_iw_i\beta_d = \tfrac{1}{2}[\beta_s - (\beta_s^2 + 4\beta_d^2)^{\frac{1}{2}}].$$

Using the normalization condition $2v_i^2 + 2w_i^2 = 1$ (true when overlapping integrals are neglected), and putting $\rho = \beta_s/\beta_d$, we get for each χ the following equation for w_i^2:

$$w_i^2 = [1 + \rho/(\rho^2+4)^{\frac{1}{2}}]/4.$$

The same equation is found for every χ, hence $w_1 = w_2 = \cdots w$; similarly $v_1 = v_2 \cdots = v$. Solution of this equation using $\rho = 26.2/34.3$ (cf. reference 16) yields the v and w values given in note 2 of Table II.

[16] The values of λ and μ in Table II for the Lennard-Jones approximation are obtained as follows: The energies of the four χ's, omitting an additive term, are given by Lennard-Jones[15] as $\mp\frac{1}{2}[\epsilon_R \pm (\epsilon_R^2 + 4\epsilon_r^2)^{\frac{1}{2}}]$, where ϵ_R and ϵ_r ($-\beta_s$ and $-\beta_d$ in Lennard-Jones' notation) are the values of the resonance integral for the C−C distances R(1.44A) and r(1.35A), respectively.[14] Using $\epsilon_r = 34.3$ kcal. and $\epsilon_R = 26.2$ kcal. (Lennard-Jones[11] gives $\epsilon_R = 26.5$ kcal. and $R = 1.43$A, $\epsilon_r = 35.0$ kcal. and $r = 1.34$A, but allowance is made here[14] for $R = 1.44$A, $r = 1.35$A), the relative energies of the four χ's have been computed by the formula just given, and the results then expressed in the form $\pm\lambda\epsilon$, $\pm\mu\epsilon$, where $\epsilon = 35.0$ kcal. according to Lennard-Jones. In this way the energies can most easily be compared with those for unconjugated double bonds of length 1.34A.

3. Calculation of Dipole-Strengths of Transitions: Effects of Conjugation and Molecule-Shape

We now proceed to the calculation of intensities. First we need to calculate Q for each transition (cf. (I,4), i.e., Eq. (4) of paper I of this series[1]). Let us begin with $N\rightarrow V_1$ in the *cis* molecule. We have

$$Q=Q_y=\int\psi_N(y_1+y_2)\psi_V d\tau. \tag{3}$$

Here the y's are the y coordinates of those two of the four mobile electrons which are initially in the shell $(\chi_2)^2$ that is broken by the transition $N\rightarrow V_1$ to give $\chi_2\chi_3$ (see Eqs. (2)). [It is readily shown that all electrons which remain in closed shells during any transition can be ignored in calculating Q.] Referring to the entirely similar case of $N\rightarrow V$ of H_2 and especially to Eqs. (9), (10) in II,[2] we see that Q of Eq. (3) becomes

$$Q(N\rightarrow V_1)=2^{\frac{1}{2}}\int\chi_2 y\chi_3 dv. \tag{4}$$

Putting in the proper expressions for χ_2 and χ_3 based on Eq. (1) with coefficients as given by Table II, we get

$$\left.\begin{aligned} &\textit{Cis}, \text{ Case I: } Q(N\rightarrow V_1)\\ &\qquad=2^{\frac{1}{2}}[\tfrac{1}{4}(y_\alpha-y_\delta)-\tfrac{1}{4}(y_\beta-y_\gamma)]\\ &\textit{Cis}, \text{ Case II: } Q(N\rightarrow V_1)\\ &\qquad=2^{\frac{1}{2}}[w^2(y_\alpha-y_\delta)-v^2(y_\beta-y_\gamma)].\end{aligned}\right\}(5)$$

Quantities like y_α in Eqs. (5) arise from integrals like $\int\phi_\alpha y\phi_\alpha dv$ occurring in Eq. (4); y_α means the value of the y coordinate of atom α in Fig. 1. Cross integrals such as $\int\phi_\alpha y\phi_\beta dv$ and $\int\phi_\alpha y\phi_\gamma dv$ for the most part appear with zero coefficients in Eq. (5). There does, however, survive the quantity $2[\int\phi_\beta y\phi_\delta dv-\int\phi_\alpha y\phi_\gamma dv]$, but this is so small that it has been omitted as negligible from Eq. (5).

It should be explicitly noted that in the normalization of χ_2 and χ_3 (cf. Table II, footnote 2), overlapping integrals have been neglected. This means that Eqs. (5) are analogous to Eq. (11a) of paper II and not to Eq. (11); but the difference is relatively small here, since the overlapping integrals are relatively small for the mobile electrons.

Equations (5) and subsequent equations can be put in a more convenient form if we use the following relations, which can be derived from inspection of Fig. 1:

$$\left.\begin{aligned} &\textit{Cis} \text{ or } \textit{trans}: y_\alpha-y_\delta=R+2r\sin\theta\\ &\textit{Cis} \text{ or } \textit{trans}: y_\beta-y_\gamma=R\\ &\textit{Cis}: \quad z_\beta-z_\alpha=z_\gamma-z_\delta=r\cos\theta\\ &\textit{Trans}: z_\alpha-z_\beta=z_\gamma-z_\delta=r\cos\theta;\\ &\qquad z_\alpha-z_\delta=2r\cos\theta;\ z_\beta-z_\gamma=0.\end{aligned}\right\}(6)$$

Using Eqs. (6), Eqs. (5) become:

$$\left.\begin{aligned} &\textit{Cis}, \text{ Case I: } Q(N\rightarrow V_1)=2^{-\frac{1}{2}}r\sin\theta\\ &\textit{Cis}, \text{ Case II: } Q(N\rightarrow V_1)\\ &\qquad=2^{\frac{1}{2}}[(w^2-v^2)R+2w^2r\sin\theta]\\ &\qquad=0.252R+0.959r\sin\theta.\end{aligned}\right\}(7)$$

Eqs. (7) show that the value of Q, hence the intensity of the transition $N\rightarrow V_1$ in cisbutadiene, is decidedly sensitive to the value of θ in Fig. 1, and also depends on r and (in Case II only) on R. Further, Q is seen to depend on w and v; the Case I equation can be obtained from the first equation of Case II by putting $v=w=\frac{1}{4}$ in the latter. Similar results will be found for transbutadiene, and for the other transitions $N\rightarrow V_2$ and so on.

Next let us calculate Q for $N\rightarrow V_1$ in transbutadiene. Here Q is in the yz plane, but is not directed along either y or z. We can determine its direction and magnitude by calculating Q_y and Q_z separately, then combining them vectorially; the magnitude of Q is then $(Q_y^2+Q_z^2)^{\frac{1}{2}}$.

The calculation of Q_y for transbutadiene proceeds exactly as for cisbutadiene and leads to just the same Eqs. (5), (7). To calculate Q_z, we replace y by z in Eqs. (3), (4), and (5). Using Eqs. (6), we get

$$\left.\begin{aligned} &\textit{Trans}: \text{Case I: } Q_z(N\rightarrow V_1)=2^{-\frac{1}{2}}r\cos\theta\\ &\textit{Trans}: \text{Case II: } Q_z(N\rightarrow V_1)=2^{\frac{1}{2}}w^2r\cos\theta\\ &\qquad=0.959r\cos\theta.\end{aligned}\right\}(8)$$

Let us consider next the transitions $N\rightarrow V_2$ and $N\rightarrow V_3$. For transbutadiene these are forbidden, so $Q=0$ for each. For cisbutadiene, Q is Q_z. We now have instead of Eq. (4),

$$\left.\begin{aligned} &Q(N\rightarrow V_2)=2^{\frac{1}{2}}\int\chi_2 z\chi_4 dv\\ &Q(N\rightarrow V_3)=2^{\frac{1}{2}}\int\chi_1 z\chi_3 dv.\end{aligned}\right\}(9)$$

TABLE III. *Q^2 values for zero conjugation (Case I) in LCAO approximation.**

TRANSITION	Q^2 VALUES	
	CISBUTADIENE	TRANSBUTADIENE
$N\rightarrow V_1$	$\frac{1}{2}r^2\sin^2\theta$	$\frac{1}{2}r^2$
$N\rightarrow V_2$	$\frac{1}{2}r^2\cos^2\theta$	0
$N\rightarrow V_3$	$\frac{1}{2}r^2\cos^2\theta$	0
$N\rightarrow V_4$	$\frac{1}{2}r^2\sin^2\theta$	$\frac{1}{2}r^2$
Total	r^2	r^2

* The table is based on Eqs. (7), (8), (10), (12), (13).

Proceeding in the usual way, neglecting overlapping integrals and small z cross-integrals, we find

$$\left.\begin{aligned} &\textit{Cis}, \text{ Case I: } Q(N\rightarrow V_2)=Q(N\rightarrow V_3)\\ &\qquad\qquad =-2^{-\frac{1}{2}}r\cos\theta\\ &\textit{Cis}, \text{ Case II: } Q(N\rightarrow V_2)=Q(N\rightarrow V_3)\\ &\qquad =-2^{\frac{1}{2}}vwr\cos\theta=-0.660r\cos\theta. \end{aligned}\right\}(10)$$

For $N\rightarrow V_4$, the polarization relations are similar to those for $N\rightarrow V_1$: we have Q_y for cis, Q_y and Q_z for transbutadiene. For cisbutadiene, we find

$$Q(N\rightarrow V_4)=2^{\frac{1}{2}}\int\chi_1 y\chi_4 dv, \qquad (11)$$

$$\left.\begin{aligned} &\textit{Cis}, \text{ Case I: } Q(N\rightarrow V_4)=2^{-\frac{1}{2}}r\sin\theta\\ &\textit{Cis}, \text{ Case II: } Q(N\rightarrow V_4)\\ &\qquad =2^{\frac{1}{2}}[-(w^2-v^2)R+2v^2r\sin\theta]\\ &\qquad =-0.252R+0.455r\sin\theta. \end{aligned}\right\}(12)$$

For transbutadiene, the results for Q_y are the same as just given by Eqs. (11), (12). For Q_z we find

$$\left.\begin{aligned} &\textit{Trans}, \text{ Case I: } Q_z(N\rightarrow V_4)=2^{-\frac{1}{2}}r\cos\theta\\ &\textit{Trans}, \text{ Case II: } Q_z(N\rightarrow V_4)=2^{\frac{1}{2}}v^2r\cos\theta\\ &\qquad\qquad =0.455r\cos\theta. \end{aligned}\right\}(13)$$

4. SPECTRA OF UNCONJUGATED DIENES AND POLYENES

Next let us consider the intensity relations as indicated by the dipole-strengths Q^2 for the hypothetical "Case I" with *no conjugation* (cf. Table III). [For the relations between Q^2 values and absorption coefficients and f values, cf. Eqs. (I,4), (I,6), (I,9).[1]] Recalling that, in the same approximation as has been used here, the transition $N\rightarrow V$ in C_2H_4 (cf. Eq. (11a) and text on C_2H_4 in II of this series) has $Q^2=\frac{1}{2}r^2$, we may first observe that the sum of the dipole strengths of our four $N\rightarrow V$ transitions in 1,3-butadiene is exactly twice that for the one transition in C_2H_4. In other words, the total dipole-strength per double bond is unaltered, although the distribution of intensity among the several transitions is seen to depend markedly on the shape of the molecule.

If Case I were rigorously realized, all our four transitions would coincide in frequency. For since in rigorous Case I the MO's χ_1 and χ_2 would have equal energy $(C-\epsilon)$, and χ_3 and χ_4 also equal energy $(C+\epsilon)$, the energy change would be $2\epsilon+\gamma$ for each of our four transitions, equal to the value for $N\rightarrow V$ in C_2H_4. Hence in this approximation the absorption spectrum should be exactly the same for 1,3-butadiene as for ethylene, except for details of fine structure and a factor two in intensity.

Actually, the double bonds in 1,3-butadiene are conjugated (Case II) and Case I is in some important respects not a good approximation. It is, however, possible to generalize from our discussion of the hypothetical Case I in 1,3-butadiene, and thereby to reach valid conclusions concerning other dienes and polyenes in which there is actually no conjugation. By a treatment similar to that used above for Case I, it is easily found that for a molecule containing any number of unconjugated double bonds, the total $N\rightarrow V$ absorption intensity per double bond, in the LCAO MO approximation, should be $r^2/2$. Also, the absorption should be located at approximately the same wave-lengths as for C_2H_4 and its derivatives.

Appearance pressure absorption curves given by J. Stark and co-workers[17] for the vapors of several dienes with unconjugated double bonds (diallyl, geraniolene, limonene, and sylvestrene: cf. Table VI) are very similar to those of compounds with just one double bond, except for a "double intensity." This is in agreement with the predictions of the preceding paragraph. Quantita-

[17] J. Stark, W. Steubing, C. J. Enklaar, and P. Lipp, Jahrbuch der Rad. und Elektronik **10**, 158 (1913); J. Stark and P. Levy, *ibid* **10**, 179 (1913).

tive absorption data by Scheibe and Pummerer[18] on diallyl ($CH_2=CH-CH_2-CH_2-CH=CH_2$) in solution lead to an f of very roughly 0.6 for the $N\rightarrow V$ absorption (cf. Table VI). This is in reasonable agreement with expectation (expected, about 0.4 or 0.5). Even rubber, whose molecules are supposed to contain from 100 to 1000 double bonds in an unconjugated chain, fits in here,[19] having no strong absorption when pure until wave-lengths near λ2000.[18]

Further, in molecules having long wave-length absorption due to conjugated double bonds or other causes, the addition or substitution of groups containing unconjugated double bonds is found to have practically no effect on the long wave-length spectrum.[19] This is in harmony with the results of the present section. Doubtless the unconjugated double bonds give rise in such cases to ethylene-like $N\rightarrow V$ absorption with a peak below λ2000.

5. Effects of Conjugation and Molecule-Shape on Spectra of Acyclic Dienes

Although the unconjugated "Case I" is not a good approximation for conjugated dienes and polyenes, it nevertheless already shows certain features which remain or become further developed in the conjugated "Case II." These features consist in the effect of the value of θ, and of the difference between cis- and trans-forms, on the distribution of intensity among the four $N\rightarrow V$ transitions (cf. Table III). Although in Case I these effects are unimportant, since the four transitions are not separated in the spectrum, they become important in Case II, where the frequencies of the four transitions are no longer all equal.

In order to see what happens in Case II, some numerical Q^2 values have been computed using Eqs. (7), (8), (10), (12), (13) with various assumptions as to the shape of the molecule. The results are collected in Table IV. For the cis-form, Q^2 values have been calculated for several values of θ (0°, 20°, 30°, of which the last is presumably not far from correct for 1,3-butadiene). In all cases, the Lennard-Jones calculated values of r and R (1.35 and 1.44A) have been used. For comparison, Q^2 values of Case I, for $\theta=30°$, are also included; these are taken from Table III but with numerical values substituted for $\sin\theta$, $\cos\theta$, and r ($r=1.34$A). The frequencies of the several transitions are also given (cf. Table II and its footnote 3).

Several predictions can be found in Table IV. These may be grouped under two headings. *First*, Table IV predicts a considerable increase in total Q^2 as a result of conjugation, the increase being smallest for small θ and for cis-forms, largest for large θ and for trans-forms. *Second*, Table IV predicts a great intensification of the longest wave-length transition $N\rightarrow V_1$ at the expense of the shortest wave-length transition $N\rightarrow V_4$ as a result of conjugation. This is especially true for the trans-form,—where, also, $N\rightarrow V_2$ and $N\rightarrow V_3$

[18] G. Scheibe and H. Pummerer, Ber. chem. Ges. **60**, 2163 (1927). C. B. Alsopp, Proc. Roy. Soc. **143A**, 618 (1934).

[19] K. W. Hausser, Zeits. tech. Physik **15**, 10 (1934); K. W. Hausser, R. Kuhn, and others, Zeits. f. physik. Chemie **29B**, 364 (1935); A. Smakula, Zeits. angew. Chemie **47**, 657 (1934).

Table IV. *Q^2 and frequency values for dienes (LCAO approximation).*

	Case I (no conjugation)[1]			Case II (conjugated)[1]				
Transition	Frequency[2]	Q^2(*cis*, 30°)	Q^2(*trans*, 30°)	Frequency[2]	Q^2(*cis*, 0°)	Q^2(*cis*, 20°)	Q^2(*cis*, 30°)	Q^2(*trans*, 30°)
$N\rightarrow V_1$	$2\epsilon+\delta+\eta$	0.224	0.898	$1.348\epsilon+\delta+\eta$	0.132	0.649	1.021	2.275
$N\rightarrow V_2$	$2\epsilon+\delta+\eta$	0.674	0.000	$2.096\epsilon+\delta+\eta$	0.792	0.699	0.594	0.000
$N\rightarrow V_3$	$2\epsilon+\delta+\eta$	0.674	0.000	$2.096\epsilon+\delta+\eta$	0.792	0.699	0.594	0.000
$N\rightarrow V_4$	$2\epsilon+\delta+\eta$	0.224	0.898	$2.844\epsilon+\delta+\eta$	0.132	0.023	0.003	0.286
Total		1.796	1.796		1.848	2.070	2.212	2.561

[1] The Q^2 values are all in A^2, that is, the values given must be multiplied by 10^{-16} in order to be in cm^2. The Q^2 values were calculated from Eqs. (7), (8), (10), (12), (13).

[2] The frequencies given (expressed in energy units) are based for Case II on the Lennard-Jones MO energies given in Table II. The quantities δ and η are added in order to allow for changes in interelectronic interaction energies on excitation (cf. e.g., reference 20 on the calculation of such interaction terms for C_6H_6). The quantity 2δ is intended to represent the singlet-triplet separation, so that $+\delta$ and $-\delta$ correspond to V and T states, respectively. Besides $+\delta$, a further quantity η must in general be included. As a simple example of an analogous atomic case, consider the transition $1s^22s^2$, $^1S\rightarrow 1s^22s2p$, ^3P and ^1P as worked out by Slater (cf., e.g., R. S. Mulliken, J. Chem. Phys. **2**, 789, 1934, Table II and its footnote *b*). Strictly speaking, a different δ and η should be used for each of the states V_1, V_2, V_3, V_4, and for Cases I and II.

TABLE V. *Semi-theoretical f values for conjugated dienes (LCAO approximation).*

	CASE I (NO CONJUGATION)		CASE II (CONJUGATED)				
				f VALUES			
TRANSITION	FREQUENCY	*f* VALUES	FREQUENCY	*Cis*, 0°	*Cis*, 20°	*Cis*, 30°	*Trans*, 30°
$N\rightarrow V_1$	57,000		46,900	0.07	0.33	0.53	1.17
$N\rightarrow V_2$	57,000		58,500	0.51	0.45	0.38	0.00
$N\rightarrow V_3$	57,000		58,500	0.51	0.45	0.38	0.00
$N\rightarrow V_4$	57,000		70,100	0.10	0.02	0.00	0.22
Total		1.12		1.19	1.25	1.29	1.39

are forbidden. Further, Table IV predicts that conjugation pushes $N\rightarrow V_1$ toward longer wave-lengths and the others, or at least $N\rightarrow V_4$, toward shorter wave-lengths, as compared with the unconjugated case.

One may ask how much reliance can be placed on the foregoing predictions, in view of the fact that they are based on a rather crude approximation. We expect, of course, that the calculated *absolute* Q^2 values are all too large (cf. II of this series),[2] but the predictions as stated above involve only relative values. After some consideration, it appears probable to the writer that both groups of predictions, or in any event the second group, can be relied on, perhaps even semi-quantitatively. Comparison with available experimental data strengthens this opinion, but also shows the desirability of careful new quantitative measurements.

A qualitative absorption coefficient curve for "butadiene" vapor (*presumably* 1,3-butadiene) has been given by Scheibe and Grieneisen,[12] covering wave-lengths down to about λ1660. Coming from long wave-lengths, the absorption begins with a broad intense region with not much structure, having its maximum at ν about 48,200. This region may reasonably be identified with $N\rightarrow V_1$. As compared with $N\rightarrow V$ of C_2H_4 with maximum probably at ν about 58,000, the shift toward longer wave-lengths is about 10,000 cm^{-1}.

Referring to Table IV, this 10,000 cm^{-1} should correspond to the difference between $2\epsilon+\delta+\eta$ (no conjugation, as in C_2H_4) and $1.348\epsilon+\delta+\eta$, or about 0.65ϵ. This gives ϵ about 15,500 cm^{-1}. This value is consistent with $\nu=58{,}000$ for C_2H_4 if we take $\delta+\eta$ about 27,000 cm^{-1} in both C_2H_4 and 1,3-butadiene.[21] We may take the value $\epsilon=15{,}500$ just obtained as a suitable empirical "effective ϵ" in estimating the relative positions of the states V_1, V_2, V_3, and V_4. The shifts in the spectrum due to conjugation should then according to Table IV be -0.652ϵ, $+0.096\epsilon$, $+0.096\epsilon$, $+0.844\epsilon$, or $-10{,}100$, $+1500$, $+1500$, and $+13{,}100$ cm^{-1} for $N\rightarrow V_1$, $N\rightarrow V_2$, $N\rightarrow V_3$, and $N\rightarrow V_4$, respectively.

[It is of interest to compare the foregoing $\epsilon=15{,}500$ cm^{-1} with values obtained by other methods. Hückel gave about 5300 cm^{-1}, Lennard-Jones[16] by a definitely improved calculation got 12,300 cm^{-1} (35.0 kcal.). Both these values are based on empirical thermal data. Goeppert-Mayer and Sklar[20] by a purely theoretical LCAO calculation for C_6H_6 with $r=1.39$A, got $\epsilon=15{,}300$ cm^{-1}.]

For comparison with experimental data, it is useful to calculate "semi-theoretical" *f* values[2] corresponding to the Q^2 values in Table IV, using Eq. (I, 9) with $G'=1$ and with frequency shifts estimated in the preceding paragraph. The results are given in Table V. The frequency $\nu=57{,}000$ cm^{-1} assumed for the case of no shift is based on an average value of the position of the $N\rightarrow V$ absorption maximum for several ethylene derivatives in the vapor state, as observed by Carr and co-workers.[21] This choice for the unshifted frequency gives somewhat too low a frequency for $N\rightarrow V_1$ of butadiene itself, but fits well the data for several butadiene derivatives to be discussed below (cf. Table VI).

Table V suggests that it should be possible to decide from the spectrum whether 1,3-butadiene and other conjugated dienes are predominantly *cis* or *trans*.

In the spectrum of butadiene vapor, after the intense maximum at $\nu=48{,}200$ cm^{-1}, the absorption falls to a very low minimum near

[20] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. **6**, 645 (1938).

[21] Data of Carr and co-workers (cf. E. P. Carr and H. Stücklen, J. Chem. Phys. **4**, 760 (1936) and previous papers) indicate a singlet-triplet separation of between 16,000 and 20,000 cm^{-1} for several simple ethylene derivatives, i.e., $\delta\approx 9000$ cm^{-1}. This is based on the interpretation of the long wave-length very weak absorption regions in these molecules as $N\rightarrow T$, where T is the triplet state corresponding to the mobile-electron V state. With $\delta=9000$, we get $\eta=18{,}000$ cm^{-1}.

$\nu = 57{,}000$ cm^{-1}, then begins to rise again but is still weak at 60,000 cm^{-1} where observations cease. This harmonizes best with Table V if butadiene exists in the trans-form. Raman data on liquid butadiene also give strong evidence that it is *trans*.[22]

[22] K. W. F. Kohlrausch and W. Stockmair, Zeits. f. physik. Chemie **29B**, 292 (1935).

TABLE VI. *Experimental data on dienes.*

SUBSTANCE[1]	STATE	OBSERVER[2]	$\nu_{max}(N \rightarrow V_1)$[3]	$f(N \rightarrow V_1)$[4, 5]	ν_{min}	$\nu_{max}(N \rightarrow V_2$ or $V_3)$[3]
CONJUGATED ACYCLIC DIENES						
Butadiene	Vapor	SG	48,200		57,000	
	Hexane soln.	Sm	46,100	0.28	50,500	
Isoprene (β-methyl-butadiene)	Vapor	St	47,000	*a*	52,000	(56,000)
	Hexahydrotoluol solution	SP	45,700	0.23		
	Hexane soln.	He	44,500	0.20		
	" "	Sm	45,400	0.27		
β,γ-dimethyl butadiene	Vapor	St	47,000	*b*	52,000	(56,000)
	Hexahydrotoluol solution	SP	44,300	(0.21)		
	Hexane soln.	He	44,200	0.24		
	" "	Sm	44,400	0.20	52,000	
α,α-dimethyl butadiene	Vapor	St	47,000	*c*	52,000	(56,000)
2,4-hexadiene	Vapor	St	47,000	*d*	52,000	(56,000)
α,δ-dibenzyl butadiene	Hexane soln.	Sm	42,600	0.30		
CONJUGATED CYCLIC DIENES						
Cyclopentadiene	Vapor	SG	44,000		49–58,000 (shallow)	
	Hexane soln.	He	42,000	0.05		
	Solution?	Ley	41,700	0.04		
1,3-Cyclohexadiene	Vapor	St	38,500	Weak (0.1?)	44,400	47,000 (strong[6])
	Cyclohexane solution	Al	39,100	0.07	45,700	(54,000)($f \approx 0.45$)
UNCONJUGATED DIENES						
Diallyl	Vapor	St	(56,000)			
	Solution	SP	(57,000)	(0.6?)		
	Hexane soln.	He				
Geraniolene; limonene; sylvestrene	Vapor	St	(56,000)			

[1] The symbols α, β, γ here refer to the C atoms in Fig. 1, and indicate where the methyl groups are substituted. Data on a number of additional substances containing double bonds are also given in references 17, 19.

[2] SG, see reference 12; St, see reference 17; SP, reference 18; He, reference 23; Sm, Smakula, reference 19; Al, Alsopp, reference 18; Ley, cf. Lowry and Alsopp, reference 26, but the citation given by the latter authors is apparently erroneous.

[3] Values in parentheses are uncertain, because falling near or usually somewhat beyond the limits of observation.

[4] All the f values given have been obtained using the following formulas: $f \approx [9/(N^2+2)^2] f_s$, with $f_s = 4.20 \times 10^{-9} \int k_\nu d\nu$ (cf. I, 19), and with $\int k_\nu d\nu$ approximated (cf. I, 3) by $k_{max} \Delta\nu$; k is the absorption coefficient for a concentration of 1 mole in 22.4 liters. The equation connecting f with f_s, where f_s is the effective f for the molecules in a solution having index of refraction N at the wave-length of the absorption band, is taken from Chako (J. Chem. Phys. **2**, 645 (1934), Eq. (12)). For hexane, N is about 1.54 in the region of the $N \rightarrow V$ absorption band. Chako's equation should give f values corresponding to molecules in the vapor state, and so to our calculated theoretical f's. The equation, however, takes account only of Lorentz-Lorenz forces, so that appreciable deviations of actual vapor f values from those given by the equation are possible for this reason.

[5] The letters *a*, *b*, *c*, *d* indicate qualitatively increasing intensity according to Stark; *b* and *c* differ only a little, *d* is perhaps three or four times as strong as *a*. Because of the method used, these results may, however, be not very reliable. The f value for diallyl is uncertain, because ν_{max} falls just beyond the limit of observation.

[6] From Stark's curves, the absorption coefficient maximum at 47,000 in cyclohexadiene appears to be about 10 times as intense as that at 38,500.

Absorption data are available also on several other conjugated dienes (cf. Table VI). Table V should be applicable to these without change, in the approximation here used, except perhaps for small shifts of frequency. The intensity data in Table VI are in many cases only qualitative. The quantitative data, permitting estimation of approximate experimental f values, are exclusively for dienes in solution. Here apparently the bands are shifted about 2000 cm^{-1} toward longer wave-lengths as compared with vapor. The vapor absorption data are given only in the form of appearance pressures, and come mainly from work of Stark and associates[17] dating from 1913.

In comparing the approximate experimental f values in Table VI with the calculated semi-theoretical values for $N \rightarrow V$ transitions in Table V, it is necessary to bear in mind that the latter are expected to be too large by a considerable factor. The best available quantitative evidence on this subject is perhaps that for O_2, where (cf. II, Table III) we found[2] a semi-theoretical f value of 0.55 and an observed value of 0.19 for the same kind of $N \rightarrow V$ transition as we have here (that is, one involving π electrons, which are essentially the same as the mobile electrons here). This would indicate an empirical correction factor $\frac{1}{3}$ to bring the LCAO semi-theoretical values to actual values.

Considering first the open-chain conjugated dienes in Table VI, it will be noticed that the solution data indicate about equal f values for butadiene and its derivatives. Since our analysis of the vapor spectrum, also Raman data on the liquid,[22] indicate that 1,3-butadiene is *trans*, it follows that the various derivatives listed are also all *trans*, at least in solution. If this is true, and if we assume $\theta = 30°$, the empirical correction factor which must be applied to the LCAO f values of Table V to give true f values is about $\frac{1}{4}$, a value which seems not unreasonable.

There exists, however, chemical evidence,[24] also evidence from molecular refractivities (cf. V), indicating that while the trans-form is the actual one in unbranched-chain derivatives (1,3-butadiene itself, 2,4-hexadiene, etc.), the cis-form occurs when the central carbon atoms (β,γ in Fig. 1) are substituted (isoprene, β,γ-dimethyl-butadiene). Stark's vapor absorption data, according to which the $N \rightarrow V_1$ absorption is much stronger for 2,4-hexadiene than for isoprene (cf. Table VI, note 5) tend to support this, since trans-forms should have much stronger $N \rightarrow V_1$ absorption than cis-forms. On the other hand, Stark's data for end-substituted and centrally-substituted derivatives alike indicate a second strong region of absorption at about $\nu = 56{,}000$, which would not be expected at all for *trans* molecules, and which was not observed by Scheibe and Grieneisen for butadiene vapor, but which could be explained as $N \rightarrow V_2$ and $N \rightarrow V_3$ if all the derivatives are *cis*. Thus the existing evidence seems to be somewhat conflicting and confused, unless we ignore one or another part of it.

On the whole, it appears most likely that butadiene and all its open-chain derivatives are actually *trans*, or sometimes a mixture of *cis* and *trans*.[25] Of course it may be that vapor, pure liquid, and solution differ somewhat in respect to relative proportions of *cis* and *trans*. The quantitative solution data in Table VI seem to show lower f values for centrally-substituted than for unsubstituted or end-substituted butadiene. It would be consistent with the f data of Table VI if the centrally-substituted derivatives are partially *cis* in solution (cf. Table VII), and partially or mostly *cis* in the liquid state as indicated by molecular refractivities (cf. VI).

Alternatively, there seem to be indications that substituted alkyl groups have a pronounced influence on absorption intensity and refractivity (cf. VI) quite aside from *cis-trans* isomerism. A possible explanation would be that the substituted alkyl groups considerably influence the angle θ, and so the intensity relations (cf. Table V). Another possible explanation is that pronounced hyperconjugation between the double bonds and the methyl or alkyl groups takes place (cf. end of Section 6; and especially IV, Section 7).

[23] V. Henri, in *International Critical Tables*, Vol. 5, p. 363 *et seq.* (Figs. 20, 25). Cf. also Figs. 21, 43, 89, 90, etc.

[24] Cf. W. Hückel, *Theoretische Grundlagen der organischen Chemie*, second edition, (Akademische Verlagsges. M. B. H., Leipzig, 1935), Vol. 1, p. 173; Vol. 2, p. 257.

[25] The fact that the diphenylpolyenes in the solid state are definitely *trans* (J. Hengstenberg and R. Kuhn, Zeits. f. Kryst. **75**, 301 (1930)) may be taken as further evidence for the *trans* arrangement in general.

TABLE VII. *Theoretical and observed f values.*

MOLECULE	ASSUMED FORM	"THEORETICAL" f	OBSERVED f
1,3-butadiene	*trans*, 30°	0.29	0.28
β,γ-dimethyl-butadiene	*trans*, 30°	0.29	0.21
	cis, 30°	0.13	
cyclopentadiene	*cis*, 20°	0.08	0.04
1,3-cyclohexadiene	*cis*, 33°	0.15	0.07

In any event, new quantitative measurements on the molecules here discussed, preferably in the vapor state and extending to considerably shorter wave-lengths than existing data, would be very desirable.

In concluding this section, reference should be made to a paper of Snow and Alsopp,[26] who have discussed the relation of ultraviolet absorption to molecular refractivity in conjugated dienes and polyenes, and who have concluded from empirical data that *cis* arrangements (in particular, ring structures) may give weaker spectra and smaller refractivity than *trans* arrangements. W. Hückel[24] has made a similar suggestion as regards refractivity.

6. CYCLIC CONJUGATED DIENES

Because of their ring structure, the cyclic dienes are necessarily *cis*. Further, the angle θ is affected by the number of atoms in the ring. In cyclopentadiene, if it is assumed that all the bonds are about equally strained away from their normal values, θ should be about 20°; in cyclohexadiene, about 33°.

The observed spectra of these two molecules (cf. Table VI) show much lower intensity for $N \rightarrow V_1$, just as we expect from Table V. The f value for cyclohexadiene is about twice as large as for cyclopentadiene, also as expected in view of the difference in θ (cf. Table V). The θ effect is confirmed by the refractivities, as we shall see in VI.

A quantitative comparison of observed and theoretical f values based on Tables V and VI is given in Table VII. The "theoretical" f values in Table VII are based on the Table V values, each multiplied by the empirical factor $\frac{1}{4}$ estimated in Section 5. The experimental f values are taken from Table VI.

[26] T. M. Lowry and C. B. Alsopp, Proc. Roy. Soc. **163A**, 356 (1937).

According to Table VII the f values for cyclopentadiene and 1,3-cyclohexadiene are quantitatively only about half as large as expected. This is not a serious discrepancy, however, since (1) all the "observed" f values are only rough, involving not only possible experimental errors but also errors of calculation (cf. Table VI, note 4), and (2) our empirical correction factor $\frac{1}{4}$ has been chosen to make "theoretical" and "observed" f agree for 1,3-butadiene on the not entirely certain supposition that the latter is pure *trans* with $\theta = 30°$.

Nevertheless, the available evidence does tend to indicate that the observed f values for the two cyclic dienes are considerably lower than the theoretical. There is also, beyond question, a very considerable shift toward long wave-lengths in the position of the $N \rightarrow V_1$ absorption regions in the cyclic dienes (especially in cyclohexadiene) as compared with 1,3-butadiene. [Some of the methyl-substituted open-chain dienes show appreciable displacements, too, but not so great as in the cyclic dienes.]

A reasonable explanation of these departures of the cyclic dienes from what we would expect for *cis* open-chain dienes with equal θ values can be given in terms of an increased conjugation, or "hyperconjugation," of a somewhat novel sort (cf. IV of this series).

7. FURTHER SPECTRA OF THE MOBILE ELECTRONS

Besides the four $N \rightarrow V$ transitions so far discussed, others are also possible for the mobile electrons. These include (1) transitions involving only the same mobile-electron orbitals χ_1, χ_2, χ_3, χ_4 as give rise to our four $N \rightarrow V$ transitions, and also (2) Rydberg series and other transitions, some of which may be moderately strong but which we shall not consider here. From the standpoint of total intensity, class (1) is unimportant, as will now be shown.

Let us consider first ethylene, then 1,3-butadiene. In ethylene, there is just one bonding and one antibonding mobile-electron MO, say χ_1 and χ_2. In MO approximation, the transition $N \rightarrow V$ corresponds to a jump of one electron from χ_1 to χ_2. This is the *only* allowed transition involving the two orbitals χ_1 and χ_2. A two-electron jump $\chi_1^2 \rightarrow \chi_2^2$ is forbidden rigorously, since the transition in respect to electronic states would be ${}^1A_{1g} \rightarrow {}^1A_{1g}$. Innumerable al-

lowed transitions exist, however, in which an electron jumps from χ_1 to an excited orbital (of Rydberg series type or otherwise) other than χ_2.

In 1,3-butadiene we start with an electron configuration $\chi_1^2\chi_2^2$ in state N, and have so far considered only four excited states V_1, V_2, V_3, and V_4. But there are many more excited states which can be obtained by juggling the four mobile electrons among the four orbitals χ_1, χ_2, χ_3, and χ_4. Among the possible states so obtainable there are—in contrast to ethylene—many to which transitions are allowed by the rigorous electronic selection rules. With cisbutadiene, in fact, *all* such transitions are allowed. For instance, $\chi_1^2\chi_2^2$, $^1A_1 \rightarrow \chi_1\chi_3^2\chi_4$, $^1B_2$ would be allowed, since $^1A_1 \rightarrow {}^1B_2$ is allowed with y polarization. To be sure, all of these transitions except the four "$N \rightarrow V$" transitions involve a two-electron jump or worse, which gives them all zero intensity if they are calculated in the manner used above. But it should be remembered that this result holds only in the MO approximation, so that actually all the other transitions may be expected to occur. However, the MO approximation is good enough (assuming "best" MO's for this purpose—as is proper—and not merely the rough LCAO MO's), so that we may reasonably expect to find most of the actual intensity in four actual transitions which can be identified as $N \rightarrow V_1$, $N \rightarrow V_2$, $N \rightarrow V_3$, and $N \rightarrow V_4$.

A reasonable expectation would be that $N \rightarrow V_1$, occurring at longest wave-lengths, would correspond fairly well to our predictions; $N \rightarrow V_2$ and $N \rightarrow V_3$ at somewhat shorter wave-lengths might also appear more or less as expected; $N \rightarrow V_4$, at still shorter wave-lengths, might, however, be rather badly mixed up with other transitions, both Rydberg and non-Rydberg in type. This mixing-up would be expected to be partly just a matter of superportion of different spectra in the same wave-length region, partly a matter of mixing of wave functions between different upper states.

8. Application of the Atomic Orbital Method

The discussion so far has been based entirely on the LCAO MO approximation. Since the evidence above and in II indicates that essentially correct predictions are obtained in this way, with the help of a suitable empirical correction factor for the absolute intensities, it seems hardly worth while to enter here upon a detailed discussion using the more cumbersome AO approximation. However, a few interesting conclusions can be obtained very simply.

In the MO approximation, eighteen distinct singlet electronic states (N, V_1, V_2, V_3, V_4, and thirteen others of the kind mentioned in Section 7) can be obtained by distributing the four mobile electrons in various ways among the four mobile-electron MO's χ_1, χ_2, χ_3, and χ_4. Of these, N, V_2, V_3 and seven others are of the state-species $^1A_1$ or ^1A_g, and the remaining eight of the state-species $^1B_2$ or ^1B_u (cf. Table I and Eqs. (2)). The symbols $^1A_1$ and $^1B_2$ apply to *cis*, ^1A_g and ^1B_u to *trans*, molecules. Corresponding to these eighteen MO states, there must exist in the AO approximation eighteen distinct singlet states obtainable by distributing the four mobile electrons in various ways among the four carbon $2p_x$ AO's ϕ_α, ϕ_β, ϕ_γ, ϕ_δ (cf. discussion preceding Eq. (1)).

Among these eighteen AO singlet states, there are only two independent "canonical" electron-pair-bond states with one mobile electron on each carbon atom. The remaining sixteen states must then be ionic. One of the two neutral canonical state structures corresponds to the usual way of drawing the bonds (cf. Fig. 1), while in the second, one mobile-electron bond goes from atom β to atom γ, the second (very weak, of course) from α to δ. Each of these structures has a wave function of the $^1A_1$ (for *cis*) or ^1A_g (for *trans*) species.

The actual wave function of state N in the electron-pair bond approximation is a linear combination of wave functions corresponding to the two canonical structures, with that of the first predominating. A second linear combination, with the second canonical structure predominating, must belong to an excited state, say X. Since the AO states N and X both belong to the $^1A_1$ or ^1A_g state-species, they can be identified only with MO states of the same species, namely N, V_2, V_3, or states of Section 7. We can of course immediately identify the AO state N with the MO state N.

The interesting point, however, is that the AO excited state X can not be identified with the first excited MO state V_1, but must be identified with V_2, V_3, or some higher MO state. This is especially interesting in view of the fact that the MO transition $N \rightarrow V_1$ is the longest wave-length, and in the trans-form by far the most intense, of the transitions from state N to the seventeen excited MO states based on mobile-electron orbitals.

Our comparison of MO and AO approximation states further shows by exclusion that the MO state V_1 must in AO approximation be of pure

ionic type. We also see that the transition $N \rightarrow X$ (AO approximation) is forbidden by selection rules for the trans-molecule, and we surmise that even for the cis-molecule it may be of zero intensity in the electron-pair bond approximation (i.e. if no ionic admixture is admitted into N or X).

Incidentally, it is possible that the AO wave function to which we have attached the name "state X" may not be a good approximation to that of any one actual state. Conceivably, for instance, the wave functions of states V_2 and V_3 might be approximately constructable as two linear combinations of those of "state X" and of another AO state of ionic type.

In any case, it is clear that in the dienes, as also in benzene (cf. Section 1), the longest wave-length *allowed* transition is to a V state of ionic AO type. [Strictly speaking, the *longest* wave-length transitions, but very weak, should in all or nearly all cases probably be intersystem transitions.] The first excited state to which transition is allowed in benzene has been shown by Sklar to be of ionic character in AO approximation; and as is shown in paper II and more in detail in V, this state is precisely of our V class, and the transition to it is very intense both theoretically and experimentally.

Although much more work must be done before the matter is cleared up, it seems likely that the following will turn out to be true: in resonating systems in which the usually assumed bond-arrangements (canonical structures) involve only neutral atoms or at least no variations in charge distribution, the excited energy levels resulting from resonance will not in general be responsible for more than weak absorption spectra. Intense spectra (giving color if they occur at long wave-lengths) will come only from transitions to ionic or partially ionic states (transitions of $N \rightarrow V$ type). These may be at longer or at shorter wave-lengths then the longest wave-length transitions to non-ionic singlet excited states.

The foregoing statement must certainly be modified in the case of resonating systems where the canonical structures include arrangements differing in charge distribution. In this case, intense transitions of the "charge-resonance" type may occur (cf. Section 1 above), but even here, transitions of $N \rightarrow V$ type may also be important (cf. detailed discussion in VIII of this series).

In conclusion, the writer wishes to express his thanks to Dr. G. W. Wheland for helpful discussion.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Ultraviolet Absorption of Nitrous Acid

In a recent number of this Journal,[1] Newitt and Outridge have expressed doubt concerning an earlier conclusion of Melvin and Wulf,[2] who attributed certain ultraviolet absorption bands in $NO/NO_2/H_2O$ mixtures to the carrier molecule HONO. It seems to me that apart from minor weaknesses in their own argument, Newitt and Outridge have apparently overlooked one series of data[3] which has an important bearing on the problem and which tends to strengthen the hypothesis of Melvin and Wulf.

The absorption bands observed by Melvin and Wulf lie in the region 26,000–32,000 cm^{-1} and form what appears to be essentially a normal progression with interval *c.* 1000 cm^{-1}, consistent with a vibration frequency in the excited state of the $-O-N=O$ group; subsidiary bands suggest another vibration interval, and a plausible interpretation has recently been suggested[3] differing in small details from that originally proposed by Melvin and Wulf. The band system described by Newitt and Outridge was obtained in explosions and flames of $NO/CO/N_2O$ mixtures and many of the bands appear to have the same wave-lengths within experimental error as those of Melvin and Wulf. It is not clear whether the bands of Newitt and Outridge were obtained in emission or absorption, or in both, but they conclude that the bands are really selectively enhanced bands of the NO_2 molecule.

Now the absorption spectra of the alkyl nitrites in the near ultraviolet[3] (alkyl = methyl, ethyl, *n*-propyl, isopropyl, *sec*-butyl etc.) are remarkably similar to that described by Melvin and Wulf. These all lie in the region 25,000–32,000 cm^{-1}, though the bands do not coincide precisely either with each other or with those of Melvin and Wulf. There can be no doubt that the source of the alkyl nitrite spectra is the molecules themselves and not NO_2, and we might with some conviction infer that the bands of Melvin and Wulf are really due to absorption by hydrogen nitrite HONO.

As far as the bands described by Newitt and Outridge are concerned it should be said that although there are noticeable coincidences of certain bands with some of those described by Melvin and Wulf, a closer inspection of the remainder suggests a lack of agreement which cannot be attributed to the possible inaccuracy in the wave-lengths. Moreover, the scheme of band centers suggested by Newitt and Outridge, although leading to a marked and regular succession of vibration intervals around 1000 cm^{-1}, does not show such a regularity in the smaller intervals, and the irregularity seems larger than could be accounted for by the possible errors in wave-length. There is no objection in principle to the scheme given by Newitt and Outridge, but it does not appear to be the same as that suggested by Melvin and Wulf.

To summarize, the band system described by Newitt and Outridge may well be due to the carrier molecule NO_2, but the balance of the experimental evidence does not seem such as to warrant a denial of the hypothesis of Melvin and Wulf.

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December 19, 1938.

[1] D. M. Newitt and L. E. Outridge, J. Chem. Phys. **6**, 752 (1938).
[2] E. H. Melvin and O. R. Wulf, Phys. Rev. **38**, 2294 (1931); J. Chem. Phys. **3**, 755 (1935).
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Further Remarks on the Solid-Liquid Equilibrium in Argon

A recent analysis[1] of the melting phenomena in argon suggests that the process of fusion is associated with an unexpectedly high maximum in the internal pressure, $(\partial E/\partial V)_T$, considered as a continuous function of V. For example, if we calculate E by summation of the interatomic potential function U suggested by Herzfeld and Goeppert-Mayer[2] over the atoms in a regular face-centered lattice (see lowest curve, Fig. 1), the curve is not steep enough at any point to give the required maximum value of $(\partial E/\partial V)_T$. One possibility that suggests itself is that the expression for U must be appreciably altered,[3] but I now feel it is more likely that the shape of the $(\partial E/\partial V)_T$ curve is due to a change in the atomic arrangement when the volume increases, and wish to suggest a (necessarily highly idealized) mechanism for the change.

The face-centered lattice of argon has a coördination number, N, of 12, but a body-centered lattice ($N=8$) would make E only slightly higher.[4] Examination shows that the *next* nearest neighbors in the body-centered lattice (which are much closer than when $N=12$) have a determining effect in bringing these curves close together.

As pointed out by Bernal,[5] there is no reason to suppose that the coördination number of a liquid is just 12 or 8—it might well have any value in between, even a nonintegral value, since the atoms are irregularly arranged, and at best only an average can be given. A system with average

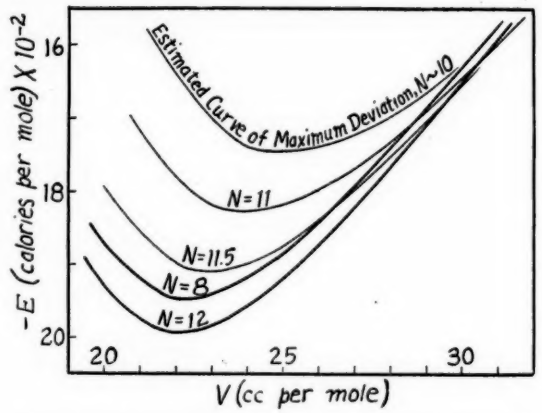

FIG. 1. Energies of various configurations. These curves do not include zero-point and thermal energies, which probably do not affect the slopes or relative positions greatly. Volume of solid =24.8, of liquid =28.0 in equilibrium at normal melting point.

$N=11$, say, could be imagined to be formed from a face-centered system in which every twelfth atom was removed, leaving a hold, the energy then being just 11/12 that of the original arrangement. Of course, further rearrangement would undoubtedly occur, so that in the end there would be more holes of smaller average size. But as long as the average coördination number remained 11, it would seem to be reasonable to accept the above estimate of the energy. But the energy is compared for similar *interatomic distances* (exclusive of distances across the holes); with the same interatomic distance, the density for $N=11$ is less than for $N=12$. If E be plotted against *molal volume*, V, the curves are displaced, as shown in Fig. 1.

With smaller coördination numbers, the holes in the lattice become larger and more numerous, allowing the next nearest neighbors of any atom to penetrate close enough to that atom to have an appreciable effect on the total potential energy. With decreasing N, the curves will, therefore, reach a maximum deviation from that for $N=12$, after which they will approach the curve for $N=8$.

When $N=8$ or 12, the atoms are all held fairly rigidly in place. Since the intermediate lattices have irregularly spaced openings, they may well be expected to have higher entropies, S. The coördination number actually attained for any given value of V is the one for which $TS-E$ is a maximum. The differences in energy between the different lattices become distinctly less as V increases, but it seems probable empirically (from a study of C_v for solid and liquid) that the differences in entropy are not so strongly dependent on V. So the state with $N=12$ will be stable at low values of V, but there will be a tendency to pass over to a state of lower coördination number, say, about 10, at larger values of V. This conceivably could be a discontinuous change, but probably, in reality, takes place over a finite range of V, producing in this range the abnormally large values of $(\partial E/\partial V)_T$ and the accompanying large values of $(\partial S/\partial V)_T$. I have remarked[6] that the occurrence of a discontinuous change of state on fusion depends on $(\partial E/\partial V)_T$ and $(\partial S/\partial V)_T$ having maxima in the same range of V. The reason that this condition is fulfilled is now obvious if the picture presented here is correct, though it should be clearly stated that the argument can apply only to cases involving van der Waals forces, while other cases, like metals, will need separate treatment.

The present theory appears to make the value of V, at which the change takes place, depend too strongly on the temperature. This may mean that the repulsive part of the energy curves should go up more steeply than indicated in Fig. 1.

I hope shortly to give a more quantitative and detailed discussion of the ideas presented in this note.

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[1] O. K. Rice, J. Chem. Phys. **6**, 472 (1938).
[2] K. F. Herzfeld and M. Goeppert-Mayer, Phys. Rev. **46**, 995 (1934); K. F. Herzfeld, *ibid.* **52**, 374 (1937), Eq. (2).
[3] O. K. Rice, Science **88**, 440 (1938).
[4] Compare London, Proc. Roy. Soc. (London) **A153**, 576 (1935).
[5] J. D. Bernal, Trans. Faraday Soc. **33**, 27 (1937).
[6] O. K. Rice, J. Chem. Phys. **5**, 492 (1937).

The Concentration of C^{13} by Chemical Exchange*

In this laboratory, the isotopes of oxygen,[1] nitrogen[2] and sulfur[3] have been concentrated successfully by chemical methods. In an attempt to concentrate C^{13}, a number of exchange reactions have been studied,[4] of which the exchange between gaseous hydrogen cyanide and sodium cyanide in water has proved to be the most promising. Experiments on this system were made in the following way: Solutions of sodium (10 to 40 percent by weight) were fed at the rate of one cc per minute into the top of a column three meters long and one cm in diameter, packed with glass spirals. Hydrogen cyanide was generated completely from the solution draining from the bottom of the column by the addition of sulfuric acid and subsequent boiling. The gas was allowed to return through the column to a water stripper and vacuum pump which maintained the system at a constant pressure (5 to 18 cm of mercury). Samples, withdrawn at intervals, were analyzed by the mass spectrometer for the ratios of carbon and nitrogen isotopes. For the carbon analysis, the hydrogen cyanide was oxidized over platinized asbestos to carbon dioxide, and for the nitrogen analysis, ammonia, obtained from the hydrolysis of the sodium cyanide, was converted to nitrogen.

Our first results showed that C^{13} concentrates in the gas phase, while N^{15} concentrates in the liquid phase to a smaller extent. However, the autocatalytic polymerization of hydrogen cyanide in solution resulted in a loss of material preventing the attainment of an equilibrium value. While this polymerization has been retarded in industrial processes,[5] by the addition of sodium sulfite to the extent of 0.1 percent of the sodium cyanide present, we have found that for the exchange reaction much larger amounts were necessary. Our best results were obtained by using a solution containing 20 percent sodium cyanide

and 2 percent sodium sulfite by weight, and by operating at a pressure of 10 cm of mercury.

Under these conditions, the column reached equilibrium in about eight hours without a trace of polymer being formed. The ratio of the carbon isotopes was changed by a factor of 1.84 and the ratio of nitrogen isotopes by a factor of 1.09 in the opposite direction. Assuming 40 theoretical plates in the column on the basis of previous experiments on the ammonia-ammonium ion exchange, the simple process factor for the hydrogen cyanide-cyanide ion exchange is calculated to be 1.015 favoring the concentration of C^{13} in the gas phase. The equilibrium constants for the exchange of carbon and nitrogen in this reaction were calculated by the method of Urey and Greiff,[6] assuming the structure of cyanide ion to be that of a gas. These calculations predict that both C^{13} and N^{15} should concentrate in the gas phase by factors of 1.026 and 1.003, respectively. This is qualitatively in agreement with the above experiments in that C^{13} shows a greater tendency than N^{15} to concentrate in the gas phase.

We are planning to use this exchange reaction to concentrate C^{13}. The cascade system of columns described by Thode and Urey,[2] modified to concentrate an isotope favored in the gas phase, should produce 46 percent C^{13} at the rate of two grams per day.

We are indebted to the Research Corporation for a grant which aided in construction of the column and analytical apparatus used in this research.

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[4] Unpublished work in this laboratory.
[5] U. S. Patents Nos. 1,856,606 and 1,950,899. We are indebted to the duPont Company for permission to use these patents.
[6] H. C. Urey and L. J. Greiff, J. Am. Chem. Soc. **57**, 321 (1935).

Vapor Pressures and Exchange Constants of Isotopic Compounds*

During the past few years a number of experiments have been made in this laboratory looking toward methods for the concentration of rare isotopes. Many of these experiments have given negative results, while others have given positive results but the separation secured was too small to make the method interesting for serious work in concentrating isotopes on a large scale. Nevertheless, these experiments may have some interest in connection with general properties of isotopic substances.

TABLE I.

TIME	TEMPERATURE	CONCENTRATION FACTOR
1 hr.	−10°C	1.06
	−40°C	1.11
½ hr.	−80°C	1.18
1½ hr.	−80°C	1.19

Distillation Methods. The Pegram column[1] was used to distill methyl alcohol to see whether it was possible to separate either the carbon or the oxygen isotopes. After a run of several days O^{18} was doubled in concentration at the bottom of the column, but C^{13} concentration was practically unchanged. The concentration secured shows that the vapor pressure of the O^{16} methyl alcohol is larger than that of the O^{18} alcohol. Formic acid was refluxed using a 1.8-meter column one cm inside diameter, packed with glass spirals for 1½ hours at a temperature of 30° to 35° with no change in the carbon concentration.

Gas Solubility Methods. Attempts were made to secure a separation by dissolving a gas in a liquid, following the general method of procedure used in this laboratory for exchange reactions.[2] CO_2-acetone exchange was carried out in the 1.8-meter one-cm diameter column with no change in the carbon concentration. The $SO_2-C_6H_5NO_2$, SO_2-CH_3OH and SO_2-H_2O exchanges were carried out in the same column with no change in concentration of the sulfur isotopes. The HCl-water exchange was carried out in an 8-meter one-cm diameter column for 44 hours at room temperature and atmospheric pressure, with a resulting slight concentration of Cl^{35} in the liquid. The ratio of concentration was changed by a factor 0.97. The C_2H_2-acetone exchange in the same column gave the results shown in Table I.

The heavy isotope of carbon concentrated in the liquid phase, but the concentration was not sufficient to be interesting as a method of separating C^{13}.

Exchange Reactions. Carbon monoxide exchange with the cuprous chloride-carbon monoxide complex in ammonia, resulted in the deposition of metallic copper and destruction of carbon monoxide. A similar result was secured when acetylene was exchanged with the cuprous chloride-acetylene complex in hydrochloric acid solution. Carbon monoxide exchanging with the cuprous chloride-carbon monoxide complex in hydrochloric acid solution using the 8-meter one-cm diameter column gave a maximum concentration factor of 1.69, concentrating C^{13} in the solution. The hydrogen sulfide exchange with sodium hydrogen sulfide solutions, using the same column, gave a concentration factor of 0.94 favoring S^{34} in the gas.

In all cases of distillation or simple solution exchanges which we have investigated, with the exception of hydrochloric acid in water (which can hardly be regarded as a simple solution exchange), the heavy isotopes of elements other than hydrogen have regularly concentrated in the liquid phase rather than the gaseous phase.

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Remarks on the Theory of Optical Activity

In a recent article Gorin, Walter and Eyring[1] have computed the rotatory power of secondary butyl alcohol, attributing it to one-electron transitions in the hydroxyl group, under a dissymmetric electrostatic perturbation from the other groups of the molecule. They imply that their method is equivalent to a method proposed by the writer,[2] differing from it only in the details of evaluation of the Born sum for the gyration parameter. We wish to point out that this is not the case. Their terms and the writer's terms represent distinct contributions to the rotatory power, and both must be considered unless it can be demonstrated that one or the other is of negligible magnitude.

The writer has shown by a simple transformation of the Born formula that the gyration parameter g, when decomposed into contributions from the component groups of the molecule, has the form

$$g = g^{(0)} + g^{(1)} + \sum_{k=1}^{N} g_k, \qquad (1)$$

where $g^{(0)}$ is a sum over pairs of groups involving the magnetic moments of the electronic centers of gravity of each group relative to the molecular center of gravity, $g^{(1)}$ is a similar sum involving the magnetic moments of each group relative to its own center of gravity, and g_k is the gyration parameter of group k, referred to its own center of gravity. If one approximates the phase of the incident light at every point in each group by its phase at the center of gravity of that group, $g^{(1)}$ as well as all g_k vanish and g reduces to $g^{(0)}$, the term considered by the writer. This is a reasonable first approximation, but its adequacy is difficult to ascertain except by detailed calculation. Gorin, Walter and Eyring, on the other hand, base their calculations on the assumption that the rotatory power is due entirely to the terms g_k of Eq. (1).

The writer's early calculation for butyl alcohol and calculations now in progress for a number of simple molecules show that $g^{(0)}$ is of the same magnitude as the experimental rotation, and in most cases agreement with experiment can be obtained with suitable internal orientation. Comparable agreement with experiment for butyl alcohol is obtained by Gorin, Walter and Eyring, using only one term of Eq. (1), the g_k of the hydroxyl group. If any of the g_k are of appreciable magnitude, there is no reason to suppose that $g^{(1)}$ is negligible. If these facts are true, one can only conclude that all terms of Eq. (1) must be considered in any calculation of optical activity.

From these remarks it is clear that the neglect of $g^{(0)}$ in the calculation of Gorin, Walter and Eyring on butyl-alcohol is entirely unjustified, since, if it is not the dominant term, it is certainly a major one. Moreover, if any of the g_k are important, their neglect of all such terms except that of the hydroxyl group seems questionable. If the alkyl groups make no contribution, it is difficult to understand how the hydrocarbon, three-methyl hexane, in which a propyl group replaces the hydroxyl, can have a molecular rotation of the same magnitude as butyl alcohol. The writer is, however, in agreement with the remarks of Gorin, Walter and Eyring concerning the influence of hindered rotation in the hydroxyl group on its optical properties. This would produce some change in $g^{(0)}$, but could scarcely alter the magnitude of its contribution.

Finally, it does not appear to the writer, that it has been unambiguously demonstrated that $g^{(0)}$ is not the dominant term in Eq. (1). The explicit quantum mechanical calculation of the g_k requires the use of such rough approximations that it can scarcely yield more than the order of magnitude of these quantities. On the other hand, it must be admitted that the writer's calculation of $g^{(0)}$ involves some uncertainty in the estimation of the optical anisotropy of the groups composing the molecule. At the present stage of the problem, one can only emphasize the necessity for careful examination of all terms of Eq. (1). In general $g^{(0)}$ will be a major term, if not always the dominant term, and its neglect cannot be justified.

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Exchange Force Transitions in Paramagnetic Compounds

K. K. Kelley[1] has recently shown that there are "humps" in the specific heat curves of MnSe and MnTe taking place at 247°K and 307°K. Similar humps had been found by Millar[2] for MnO and MnS which occurred at lower temperatures (116°K and 140°K). No explanation of these humps has been offered and it is the purpose of this note to show that they arise from the existence of an exchange force on the low temperature side.

The author[3] has measured the paramagnetic susceptibility of MnO from 14°K to 298°K and the paramagnetism drops to nearly diamagnetism upon lowering the temperature through the transition hump. This means that electron spins giving rise to paramagnetism at the high temperature are no longer free to orient themselves at the low temperature. In other words, there has been a spin coupling effected and this gives rise to an exchange force. The new binding force has the effect of drawing the atoms together and this has been observed by B. Ruhemann.[4] The specific heat is proportional to the expansion coefficient and hence there is the observed hump or additional specific heat which has been observed.[1, 2] We may therefore conclude that at low temperatures part of the lattice binding energy is due to a negative exchange integral and as the lattice energy increases this becomes a positive exchange integral.

The change of sign of the exchange integral for electrons in the $3d$ shell of Mn can be understood by the recent remarks of Pauling[5] in which it becomes clear that interatomic exchange forces can arise from such electrons. The author will measure the predicted transition effect in the paramagnetic susceptibility of MnSe and MnTe. There should also be an expansion of these crystals at the transition temperature.

The transition temperature is higher, the higher the

atomic number of the combining element with the Mn. We may understand this by the following argument: The exchange force energy is nearly the same for all the compounds (MnO, MnS, MnSe, MnTe) and the perturbing energy needed to destroy this extra binding is also the same. Now in order to get a crystal with heavy elements into the required high energy state (lattice vibration) it requires a higher temperature than for a lighter crystal. This is considering the question from a Boltzmann statistical view point i.e., the number of heavy elements in a given high energy state is less than the number of lighter ones in such a state for a given temperature.

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The Raman Spectrum and Vibrational Frequencies of Methyl Acetylene

The Raman spectrum of liquid methyl acetylene has been measured in connection with the research program on molecular vibrations now in progress in this laboratory. The apparatus used has been previously described;[1] the blue-violet mercury lines were used for excitation. The material was made available through the kindness of Professor G. B. Kistiakowsky. It was of extreme purity, having been prepared for use in the hydrogenation calorimeter; the preparation will be described in a future publication of the series on heats of hydrogenation.

The observed shifts are given in Table I, together with their intensities, polarization characters, and assignments.

TABLE I. *Observed Raman shifts.*

$\Delta\nu$, cm^{-1}	EXCITATION*	INTENSITY, POLARIZATION†	ASSIGNMENT
333	*e, k, i*	10 *b, D*	*E* fund.
642	*e, k, g, i*	4 *b, D*	*E* fund.
926	*e, k, i*	6, *P*	A_1 fund.
1035	*e, k*	0, —	*E* fund.
1380	*e, k*	2, *D*?	A_1 fund.
1444	*e, k*	2, —	*E* fund.
2125	*e, k, f, g*	12, *P*	A_1 fund.
2735	*e, k*	1, —	$1380^2 = 2760(A_1)$
2866	*e, k*	3, —	$1444^2 = 2888(A_1+A_2+E)$**
2927	*e, k*	8, *P*	A_1 fund.**
2975	*e, k*	2, —	*E* fund.
3300	*e, k*	3, —	A_1 fund.

* K. W. F. Kohlrausch's notation for the mercury lines is used: $e = 22938$, $f = 22995$, $g = 23039$, $i = 24516$, $k = 24705$ cm^{-1}.
† *b* = broad, *P* = polarized ($\rho \leq 6/7$), *D* = depolarized ($\rho = 6/7$).
** Resonance doublet.

TABLE II. *Fundamental frequencies of methyl acetylene.*

A_1	*E*
926	333
1380	642
2125	1035
2910	1444
3300	2975

The polarizations of the lines have not been previously studied, nor has the 1035 cm^{-1} shift been previously reported. Other shifts agree with those found by Glockler and Davis.[2]

The symmetry of the molecule (C_{3v}) yields the structure $\Gamma = 5A_1 + 5E$ for the representation formed by the normal coordinates. The selection rules allow both the non-degenerate (A_1) and degenerate (E) fundamentals to appear in the Raman effect; the A_1 fundamentals may be polarized. These considerations lead immediately to the assignment given in Table I, with the set of fundamentals shown in Table II. This assignment differs in several respects from that given by Glockler and Davis.[2] The figure of 2910 cm^{-1} for the symmetrical C−H stretching frequency in the methyl group results from an arbitrary allowance for the effect of the resonance interaction with the overtone of the 1444 cm^{-1} fundamental. The presence of this interaction is shown by the intensity of the overtone.

Low temperature heat capacity measurements were made on the gas by Mr. W. W. Ransom, using the "hot-wire" method as developed in this laboratory.[3] The experimental values agree, within experimental error, with those calculated from the fundamental frequencies of Table II. (At 158°K, calculated value 8.247, observed value 8.24 cal./mole/degree; at higher temperatures the experimental data are as yet incomplete.)

A complete report, including thermodynamic calculations, will be published when a study of the infra-red absorption, now in prospect, has been completed.

In conclusion, I wish to express my thanks to Mr. Ransom for the use of his heat-capacity measurements, and especially to Professor E. B. Wilson, Jr., for suggesting the study of this molecule and for his continued interest in the work.

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